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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY

PLANT AND MACHINERY.

By J. H. WEST, M.I.Chem.E., A.M.Inst.C.E

AGAIN the past year has been characterised by severe depression in the chemical industry, though signs of renewed activity are just beginning to appear in the last few months. During such periods manufacturers have little incentive to instal new plant, or to replace obsolete apparatus by more modern types, and it is also difficult to find money for the commercial development of new inventions.

While few, if any, fundamentally new ideas are available for record, there is no doubt that steady and important progress is being made in the task of placing the design of chemical plant upon a scientific basis.

The founding of the Institution of Chemical Engineers is an event of the highest importance, not only from the point of view of a new and authoritative centre for the collection and dissemination of scientific information on the design of chemical plant, but also because the Institution will exercise a much-needed control over the status and qualifications of chemical engineers in this country, and will do much to counteract the harm which has been done in the past by incompetent persons who undertook the design of plant without having the training and experience necessary for this work. The work of the Institution will not conflict with or overlap the excellent work which is being done by the Chemical Engineering Group of the Society in the holding of conferences and publication of papers on chemical engineering subjects, since these usually refer to commercial developments, whereas the papers presented to the Institution may be expected to be of a more scientific character.

Another important event of the past year is the foundation

of the Ramsay Memorial Chair of Chemical Engineering at University College, London, the first full professorship in this subject to be established in the country. Both as regards the training of chemical engineers and the carrying out of research this foundation should have important results.

The most novel and interesting item in this section which has appeared during the past year is Dr. H. S. Hele-Shaw's "stream-line filter," which consists¹ of a large number of sheets of paper perforated with holes and pressed together under an adjustable pressure, so that the holes in register form tubes. In the commercial filter unit the size of the sheets is roughly 8½ in. by 6½ in., and there are 32 inlet holes ¼ in. in diameter, and 53 outlet holes ⅜ in. in diameter. Arrangements are made in the end plates, or heads, of the press for connecting the inlet and outlet holes or tubes, respectively, together. On pumping the liquid to be filtered into the inlet tubes the solid matter is retained and the clear filtrate passes between the sheets of paper to the outlet tubes. So minute is the spacing between the sheets of paper when pressed together that really extraordinary feats of filtering can be performed without any tendency to clogging occurring or the rate of flow diminishing under constant pressure. Dirty black oil from the crank case of an engine comes out clear and light in colour, and cloudy ditchwater containing matter which will remain almost indefinitely in suspension, emerges perfectly colourless and clear. For the clarification of oils and varnishes and the removal of colloidal suspensions in liquids this filter offers a new weapon which should prove very valuable. In such cases the filtrate is the valuable portion, the solids—usually a very small percentage of the whole—being thrown away. The removal of the solids from the filter can be done by slackening off the pressure on the sheets and reversing the flow, or by means of jets in the inlet tubes. While the commercial handling of filtering problems in which the solids are the valuable portion has not yet been completely solved in this filter, the solution is now within sight and only a matter of a little further experimentation.

The paper used is water- and oil-proof, and is not attacked by dilute acids, and quite recently a new type of paper has been adopted which is highly resistant to alkalis, so that the commercial filtration of 10% caustic soda solution can now be carried out satisfactorily. This is a very important advance, since hitherto the filtration of strongly alkaline solutions has been practically impossible, and settling has had to be resorted to.

In connexion with evaporation there is some prospect of the so-called "heat pump" coming into more general use in this

¹. 1923, 353T: *Proc. Roy. Soc.*, 1923, A103, 556; J., 1923, 751A.

PLANT AND MACHINERY.

country. There has in the past been considerable prejudice against this type of evaporator among English chemical engineers, but with improved construction the results now attainable command attention in view of the high evaporative efficiency per pound of live steam used. The Prache and Bouillon evaporator, which has been in use for many years on the Continent, is now being made in this country, and some idea of the results it gives may be of interest. The heat pump in this apparatus is an injector of special design giving a very large entrainment of vapour with the live steam. In order to keep down the heating surface within reasonable limits, and yet work with a small temperature drop, mechanical circulation by means of impellers is usually resorted to, thus ensuring thoroughly turbulent flow in the heating tubes and a reduction of the film resistance.² With this evaporator in single effect about $3\frac{1}{2}$ lb. of water is evaporated per lb. of live steam, or approximately as much as is obtained in a quadruple effect of the ordinary type. It is claimed that frothing is entirely eliminated, and that difficult liquids, such as milk, wool-scouring liquors, and glue liquors, can be successfully dealt with.

Another form of heat pump is the Testrup drum dryer, which has been applied to the drying of peat.³ In this case the vapour given off from the wet material on the outside of grooved drums is compressed mechanically and returned to the interior of the drums. The same principle is being applied in other dryers, both of the stationary and rotating types.

There are a number of patents connected with drying, but they mostly refer to improvements in details of construction, or to means for recovering the heat of the exit gases. The Fusion patent rotary retort, to which reference was made in last year's Report, has undergone some modification.⁴ Instead of hammers suspended from a shaft passing through the rotating tube, there is now a tumbler, comprising three or more (usually six in the latest type) radial arms, and made up of a number of sections placed end to end. The tumbler sections rest on the bottom of the rotating tube and are carried round with it until they overbalance and fall over. This retort can be used for drying, particularly where a certain amount of crushing is necessary to avoid caking and agglomeration, and also for calcining and retorting shales and lignites.

A good many patents relating to crushing and grinding have appeared. Most of these refer to improvements in detail of known forms of ball mills, disintegrators, and so forth, and call for no special comment. Grinding to extreme fineness continues to

² Proc. Chem. Eng. Group, III. & IV., 132-135; *The Power Engineer*, Sept., 1923.

³ E.P. 191,812; *J.*, 1923, 387A.

⁴ E.P. 201,966; *J.*, 1923, 1006A.

receive attention. A Plauson mill for dry grinding *in vacuo*⁵ claims the reduction of the particles to a diameter of less than 0·008 mm. This mill comprises a shaft carrying beater bars, mounted eccentrically in a double-walled casing, the space between the walls being used for the circulation of a heating or cooling fluid. A sieve on the outlet pipe stops the coarser particles from reaching the settling chamber and returns them to the mill, while an ultra-filter prevents the finely ground material from reaching the vacuum pump. The material to be ground is fed in through a hopper and an air-lock comprising two valves coupled together so that when one is open the other is shut. Means are provided for removing the finest material from the settling chamber without breaking the vacuum.

Another mill for producing very fine powders is that of E. Podszus.⁶ In this the attrition is produced by the crushing and rubbing of fine particles between impinging coarser particles of the same material, the coarser particles being added in the ratio of 1 to 2 of fines. Two combined fans and beaters rotate at high speed in opposite directions on shafts with the same horizontal axis, and thereby cause the particles to impinge on one another. The solid material occupies about one-third of the space in the casing, and the rest may contain air or liquid. The ground material is blown out by compressed air, with a device for returning the coarser particles to the mill, and a filter on the outlet of the collecting box to retain the fine powder. It is claimed that this mill can grind to colloidal fineness, and that the wear on the mill is very small.

As regards distillation there are no new features of importance to be found in the year's patents, but several papers of interest have appeared. Vols. III. and IV. of the Proceedings of the Chemical Engineering Group, recently published, contain three papers on distillation—"The design of ammoniacal liquor stills" by P. Parrish,⁷ "Tar distillation" by W. A. Walmsley, and "Glycerin distillation" by T. H. Gray.⁸ Calculations for fractionating columns are considered in two papers,⁹ and a theoretical treatment of the condensation of vapour from mixtures of vapour and non-condensable gas is given by B. F. Dodge.¹⁰

The very important subject of heat transference is dealt with in two papers—by G. J. Greenfield,¹¹ and B. Heastie.¹² The

⁵ E.P. 195,690; *J.*, 1923, 534A.

⁶ E.P. 183,134; *J.*, 1923, 385A.

⁷ *J.*, 1922, 229T.

⁸ *J.*, 1922, 281R.

⁹ *J.*, 1923, 37A, 533A.

¹⁰ *J. Ind. Eng. Chem.*, 1922, 14, 1062; *J.*, 1923, 38A.

¹¹ *Chem. and Ind.*, 1923, 390.

¹² *J.*, 1923, 443T.

atter is a valuable paper, giving both theoretical and practical treatment of the subject. One interesting practical point brought out is that the use of superheated steam in a heater may give worse results than those obtained with saturated or even exhaust steam, owing to the resistance of the gas film on the heater wall when superheated steam is used. The value of this paper would have been considerably greater if references to the previous work quoted had been given.

A great deal of work is being done on the electrical precipitation of dust, as is shown by the fact that over fifty patents relating to it have been abstracted in the *Journal* during the year. Most of these refer to different forms and constructions of electrodes, and mechanical devices for removing the dust from the electrodes. Others relate to the nature of the electrical field employed, several proposing an alternating field superposed on a direct current field.¹³ Another proposal is to use electrodes of thin cross-section which are heated electrically so as to ionise the gas, and at the same time serve as discharge electrodes.¹⁴ One patent¹⁵ proposes to subject the dust to the action of Röntgen rays whereby the particles become positively charged and are then precipitated electrically.

On the other hand, several methods of preventing ionisation of the gas before treatment, or removal of any ionisation due to flames, are described.

The addition of finely divided granular material to the gas before treatment in order to assist in bringing down the fine dust is proposed,¹⁶ and also the addition of acid fume.¹⁷

Leaching is an operation which is usually regarded as so simple as not to require scientific study, but the paper by F. G. Donnan¹⁸ shows that it is capable of mathematical treatment and reduction to scientific formulae. This class of paper, to which belong also the contributions of M. B. Donald and C. W. Tyson to the Institution of Chemical Engineers,¹⁹ on absorption towers and conditions of constant flow in filter presses, is very valuable, since every attempt to analyse the fundamental principles which underlie chemical operations must be welcomed. Practical designers of plant may scoff at these mathematical investigations as not taking actual working conditions sufficiently into account, but gradually theory

¹³ G.P. 369,879. *J.*, 1923, 536A. G.P. 358,307; *J.*, 1923, 130A.

¹⁴ G.P. 364,436; *J.*, 1923, 433A. E.P. 197,857; *J.*, 1923, 696A.

¹⁵ G.P. 376,096; *J.*, 1923, 1008A.

¹⁶ U.S.P. 1,446,778; *J.*, 1923, 340A.

¹⁷ U.S.P. 1,440,886; *J.*, 1923, 169A.

¹⁸ *J.*, 1923, 440T.

¹⁹ *J.*, 1923, 1209A.

and practice will be brought closer together, with the result that the design of chemical plant will reach as sound and scientific a basis as that of mechanical engineering design.

Among miscellaneous matters mention may be made of a number of papers dealing with the causes of explosions in chemical works,²⁰ explosions in air liquefaction apparatus,²¹ and dust explosions.²² The efficiency of different types of agitators is a subject which has received too little attention, possibly owing to lack of methods for making accurate comparisons. E. V. Murphree has developed a method depending upon the rate of solution of crystals.²³ The volume of the solution, the weight and size of the crystals, and the rate of solution are determined, and from the data the constant K_1 , representing the weight in grams dissolved per sq. cm. of surface of crystals per minute per unit concentration difference, can be calculated.

High-speed agitation as an aid to reactions between gases and liquids has been studied by C. H. Milligan and E. E. Reid.²⁴ The agitator, which consisted of a perforated disc with a bell-shaped projection beneath, could be run at speeds up to 14,000 r.p.m., and the gas was delivered beneath the agitator bell. The speed of reaction was found to vary directly with the speed of agitation.

A novel form of agitator for mixing liquids of different densities is patented by F. De Dietrich.²⁵ It is of elongated egg shape and hollow, the small end reaching almost to the conical bottom of the vessel and having there an orifice through which the heavier liquid enters it. Owing to the rotation of the vessel the liquid, both inside and outside the agitator, rotates also, and the heavy liquid inside the agitator rises by centrifugal force till it reaches a series of orifices at the widest part of the agitator near the top, through which it is thrown in fine drops which sink through the lighter liquid.

The combined action of centrifugal force and an electrical field for removing colloid impurities from liquids, such as used transformer oil is advocated by A. Marx and J. Rozières.²⁶ One pole of the electric supply is connected to the rotating bowl of a centrifuge and the other to a metallic cylinder placed concentrically inside the bowl, a pressure of 40,000 volts being used with electrodes 10 cm. apart.

²⁰ Z. angew. Chem., 1922, **35**, 657; J., 1923, 1A.

²¹ Ibid., 1923, **36**, 262; J., 1923, 587A.

²² Chem. Age, 1923, 8, 54; J., 1923, 211A. Ind. Eng. Chem., 1923, **15**, 232; J., 1923, 339A. Kolloid-Zeits., 1923, **33**, 101; J., 1923, 873A.

²³ Ind. Eng. Chem., 1923, **15**, 148; J., 1923, 253A.

²⁴ Ibid., 1923, **15**, 1048; J., 1923, 1159A.

²⁵ U.S.P. 1,464,150; J., 1923, 1114A.

²⁶ Comptes rend., 1923, **176**, 1396; J., 1923, 637A. Chim. et Ind., 1923, **10**, 218; J., 1923, 1005A.

An interesting investigation on the effect of 38 different chemical liquids upon six kinds of wood used for making tanks has been made by S. J. Hauser and C. Bahlman.²⁷ The absorptive capacity for the different liquids, production of discoloration and taste in the liquids, and corrosion were tested for each kind of wood, and the results set out in graphs.

E. Passburg and H. Griffiths have patented a rocking trough apparatus²⁸ for obtaining large and uniform crystals. Mention was made of this in last year's Report, but no reference was given.

²⁷ *Chem. and Met. Eng.*, 1923, **28**, 159; *J.*, 1923, 211A.

²⁸ E.P. 204,559; *J.*, 1923, 1161A.

FUEL

By EDGAR C. EVANS, B.Sc., F.I.C., M.I.M.E.

Messrs. Sutcliffe, Speakman and Co., London.

THE continued economic depression in England has hampered large-scale developments in fuel technology in this country during the past year. A considerable amount of work has been done on the laboratory and semi-commercial scale, but no new developments of a far-reaching character can be said to have taken place. At the same time, other countries more favourably circumstanced have inaugurated large-scale schemes which promise to be of considerable importance in the future in the rational utilisation of fuel.

A general survey of the published work during the past twelve months serves to emphasise in a very interesting manner the divergencies that exist in different countries between the standpoints from which they regard the fuel question. Problems that are of supreme importance in England are frequently only of superficial interest to other countries. On the other hand, a study of continental and American work emphasises the importance that is laid there on aspects of the subject, which are in this country regarded as having only a theoretical interest. These divergencies are due to a number of reasons, some of them economic, some of them due to the character of the fuels available, and others to purely social customs, to methods of fuel utilisation which have become almost traditional. In England the universal use of the open fire (essentially a wasteful and unscientific method of domestic heating) has caused particular emphasis to be laid on the production of a smokeless fuel. Many attempts have been made to solve this problem, but the difficulties experienced have been so great that it has taken over 20 years of work to bring within sight a solution of the problems involved. In this long period of experimentation considerable research has been done which will probably be of very great ultimate importance to the fuel industry, and yet, despite this, our views of smokeless fuel production have received considerable criticism from continental observers.¹ This criticism in itself is indicative of the difference in the continental viewpoint from our own in so far as fuel research is concerned. Considerable attention appears to have been given in the continental research stations to

¹ E. Audibert, *Revue de l'Industrie Minerale*, No. 53, March 1, 1923.

the production of oil from coal, and the solid residues of coal distillation have frequently been a matter of secondary importance, whereas the by-products are of primary value. For this reason such processes as the Bergius process, which gives a very high yield of liquid distillates, have received far greater attention than they have had in this country, and similarly the tendency of continental research has been to concentrate more on the character of the oils, tars, and other by-products obtained in the distillation of coal at various temperatures.

These national tendencies, however, are really helpful; they enable a far wider field to be covered than would be possible if a purely individualistic view were taken, and an annual review of this type allows of the co-ordination of the various aspects of the work that is being done, and to some extent linking up the apparently divergent researches into a systematic whole.

But, whilst there are many aspects of fuel technology which are national (in the narrow sense), in their importance, there are others which are international—they affect every fuel-producing or fuel-using country to a greater or less extent.

The most important of these is undoubtedly the use of fuel for steam raising, but unfortunately this aspect of the question has—to its detriment—left the domain of the chemist almost entirely for that of the engineer, and it, therefore, participates only to a limited extent in a modern review of the progress of applied chemistry.

A question, however, which is of vital importance in practically every industrial country, is that of fuel consumption and utilisation in the iron and steel industry, and for that reason a big proportion of the world's work in fuel technology is associated with one or other of the various branches of the iron and steel and metallurgical industries. During the past twelve months a considerable amount of work has been published in connexion with the properties of blast-furnace coke, particularly with reference to the influence of structure of the coke on its combustibility. The work that has been done in this direction links up in a very interesting manner the conflicting claims of high- and low-temperature carbonisation, and brings into line the interests of the two great coal-consuming industries—the gas and coke industries—with those of the industrial and domestic consumer.

In the light of recent work on this aspect of the fuel question, it is possible to visualise a large-scale process of carbonisation at gradually increasing temperatures in which a high gas yield is obtained at the same time as a high yield of liquid products, in which a maximum yield of ammonium sulphate is obtained with a maximum of motor spirit, and which results in a hard, dense, solid fuel possessing physical qualities which make it pre-eminently

suitable for blast-furnace work whilst, at the same time, it has a combustibility of an order sufficient to allow it to be used as a domestic fuel.

Such a fractional distillation of coal is already in use on a large scale in certain coalfields, and it is probable that the future will see a rapid extension of this principle, with the result that much of the research which is now a matter of academic interest will become of very considerable economic importance to the great fuel-consuming industries.

FUEL ECONOMY.

From the general standpoint of fuel economy, it is pleasing to note that the average fuel consumption per unit of electricity produced in power stations in this country is being consistently reduced. From a return issued by the Electricity Commissioners in 1923,² the power production in 1922 showed an increase of 807 million units or 17.5%; the fuel consumption showed an increase of 203,637 tons or only 3% over the preceding year, whilst the average fuel consumption per unit of electricity generated was reduced from 3.11 lb. to 2.78 lb. The possibility of further improvement, however, is shown by the achievement of the North Tees Station of the Newcastle-on-Tyne Electric Supply Co. of producing electricity with a fuel consumption of only 1.73 lb. of coal per unit—a remarkable result.

POWDERED FUEL.

The subject of powdered fuel in steam boilers continues to receive attention. H. Kreisinger and J. Blizzard give results obtained in tests at two American plants.³ One of the plant's mentioned, installed at the Lakeside Station of the Milwaukee Electric Railway and Light Co., is particularly interesting. This furnace has a water screen connected with the boiler which acts as an absorber to some extent of the heat radiated from the bottom of the furnace. The furnace also is hollow-walled, which reduces radiation losses, and the furnace air is heated to a temperature of about 230° C. The overall efficiency of the boiler and economiser is over 90% of the net calorific value of the fuel.

D. Brownlie⁴ gives further particulars of this plant and adds some valuable data regarding labour costs, auxiliary power consumption, maintenance cost, and capital costs of powdered fuel firing. He advocates the use of pulverised low-temperature coke for steam raising.

²H.M. Stationery Office, White Paper, March, 1923.

³Colliery Guardian, Feb. 2, 1923, pp. 263-264.

⁴Trans. Inst. Elect. Eng., Oct. 3, 1923 (Advance copy).

J. T. Dunn⁵ gave comparative figures or costs of powdered fuel and solid fuels for reheating furnaces at a British steel works, which illustrate the advantages of powdered fuel for this type of work.

J. S. Atkinson⁶ in a general paper draws attention to various aspects of powdered fuel production and utilisation, including preliminary drying, grinding, combustion, and ash handling.

In connexion with the utilisation of pulverised low-temperature coke for steam raising, the Ford Motor Co. of Canada is building at Detroit a plant with an initial capacity of 400 tons per day, which ultimately is to be increased to 2400 tons per day. Of this it is proposed to use 1800 tons for the boilers, while 600 tons will be used in the production of briquettes for domestic and industrial purposes.⁷

PEAT.

Whilst not of outstanding commercial importance in England, the question of the production of a high-grade fuel from peat has considerable potentialities in other countries and work is being actively pursued in many directions. The question is important in Canada owing to the dependence of the industrial sections of Ontario and Quebec on fuel imported from the United States. In an interim report of the Canadian Dominion Fuel Board⁸ surveys of peat resources amounting to approximately 200,000,000 tons are mentioned. An outline description is given of a method of producing air-dried peat, and a scheme is contemplated of 20,000 tons per annum capacity.

The Fuel Research Board has issued an exhaustive report on the production of air-dried peat⁹ containing the results of investigations by E. J. Duffy and P. F. Purcell on the air-drying of peat in this and other countries. A pessimistic view is taken of the possibilities of the drying of peat by heat.

J. W. Hinchley¹⁰ gives particulars of some interesting work on the reduction of moisture in peat by pressure. After warming to the boiling point of water, suitably applied pressure rising to $\frac{1}{2}$ ton per sq. inch reduced the moisture content to 35% to 50% with different peats. With cold-pressing of Somerset peat the percentage of moisture left was 75%, but with hot-pressing this was reduced to 50%. Further drying to 30% moisture could be effected by waste heat. Calculations are made of the energy

⁵ *Iron and Coal Trades Review*, April 13, 1923.

⁶ *Ibid.*, Dec. 22, 1923.

⁷ *Chem. and Ind.*, 1923, 1166.

⁸ *Iron and Coal Trades Review*, July 13, 1923.

⁹ H.M. Stationery Office, 1923.

¹⁰ *J.*, 1922, 365t.

consumption of the process, and estimates of the cost of plant and of operations are given.

J. C. Morrison¹¹ subjects the peat to pressure and suction to reduce the moisture from 80% to 50%. The semi-dried peat is then further dried to about 20% of moisture by hot air and subsequently briquetted. In a private communication to the writer the inventor claims to have proved the process commercially, and states that the cost of a complete plant is approximately \$150,000 for a unit having a capacity of 100 tons a day.

LIGNITE.

The subject of the utilisation of lignite is receiving considerable attention in many countries. The French Commission on Carbonisation¹² has examined the French resources in lignites, and states that systematic work is being performed on the lignites of that country.

W. A. Bone¹³ records results of carbonising tests on air-dried lignite (30% moisture) at various temperatures. Carbon dioxide and steam were evolved below 375° C., methane and unsaturated hydrocarbons between 375° and 500°. Hydrogen was not produced until a temperature of 500° was reached. The first oil was obtained at 375°. He suggests that the intensity of combustion of the lignite be increased by subjecting it to a preliminary heating below 400°.

These results are, of course, characteristic only of the lignites examined, as lignites differ so considerably from one another. For example, in a test made by the writer on Czechoslovakian lignite, oil was evolved at a temperature of only 238° C., and at 330° a quantity equivalent to nearly 9 gallons per ton had been given off.

In a later report on Moorlands lignite¹⁴ laboratory and large-scale tests on this material are described. Dust-firing trials on about 4 tons of fuel gave disappointing results, and difficulty was experienced in securing the complete combustion of the fuel when in suspension.

C. Engelshardt¹⁵ describes an interesting gas producer using lignite as a fuel. A fuel column of only 80-100 cm. was used with an ash zone of 5-20 cm. and a combustion zone of 20 cm. To overcome the disadvantage of crumbling to powder which occurs with some lignites on drying, it was found preferable to work with the wet material and to dry the gas produced.

¹¹ U.S.P. 1,450,102; *J.*, 1923, 438A.

¹² *Iron and Coal Trades Review*. May 11, 1923.

¹³ *J. Roy. Soc. Arts*, 1923, 208; *J.*, 1923, 255A.

¹⁴ *Iron and Coal Trades Review*, Sept. 7, 1923.

¹⁵ *Z. angew. Chem.*, 1923, 36, 98; *J.*, 1923, 256A.

OIL SHALES AND LIQUID FUEL.

The subject of liquid fuel is a vitally important one in the political economy of most countries, and the chemical aspects associated with its production and utilisation are worthy of serious attention.

The question of oil shale distillation is growing in interest, and chemists in different countries are investigating the problems associated with oil shale treatment. The future importance of these materials can be gathered from the statement by R. H. McKee¹⁶ that one field, alone in the United States would yield eight times the total production of that country since the first oil well was sunk. In this article he reviews the liquid fuel situation from an oil-shale standpoint, and summarises some of the work done on the subject. He points out a fact that cannot be too frequently emphasised, that the retorting of each shale is a separate problem, and considers that the large-scale retort suitable for handling American shales has yet to be evolved. On the experimental side, the researches of R. H. McKee and R. T. Goodwin¹⁷ had shown that shale distillation was endothermic and there was absorption of heat averaging about 160 B.Th.U. per pound of shale. No fractional distillation of the shale took place, but the first product expelled was a semi-solid bitumen which by subsequent cracking yielded oil. These authors obtained a product intermediate between the kerogen of the shale and shale oil by distilling oil shale under reduced pressure. This was a highly unsaturated material, but by heating at atmospheric pressure it became more saturated. Alternatively when the shale was distilled at atmospheric pressure, the oil was much more saturated, shale thus behaving in exactly the reverse way to petroleum.

Much work has also been done on retorting processes, but up to the present no new development has taken place to merit any detailed attention. A big step forward has been taken by the recognition that every shale presents its own problem, and it is probable that two or three different types of retorts will ultimately be required to deal with the specific types of shale that exist.

Renewed attention has been given during the past year to the hydrogenation of oils and solid fuels. H. G. Shatwell¹⁸ gives a brief review of the subject with an excellent series of references to patents and publications dealing with this important question. The primary work, of course, was done by Bergius, and this process was reviewed by J. I. Graham and H. G. Shatwell.¹⁹ The hydro-

¹⁶ *Chem. and Ind.*, 1923, 193.

¹⁷ *Ind. Eng. Chem.*, 1923, 15, 343; *J.*, 1923, 483A. See also M. J. Gurvin, U.S. Bureau of Mines Bull. 210, 1922, 179-189.

¹⁸ *Fuel*, 1923, 2, 229.

¹⁹ *Fuel*, 1923, 2, 54; *J.*, 1923, 341A.

genation of coal by the Bergius process has, as yet, only been performed on a semi-commercial scale. It is possible, however, to treat coals containing less than 85% of carbon at a temperature of approximately 400° C., and pressures of 40 to 200 atm., with a production of saturated hydrocarbons similar to petroleum distillates, together with phenolic compounds, which carry most of the oxygen present in the coal. In the treatment of coal the operation is performed in two stages. In the first stage a mixture of two parts of raw coal and one part of oil is hydrogenised, resulting in the production of 87% of oil, the remaining 13% being gas and loss; 50% of this oil is used to treat a further quantity of coal, whilst the remainder is "Berginised" separately. The ultimate result from one coal tested was the production of 81% of "Berginised" products of an average density of 1.047, of which 27.2% has a density of 0.917 and a boiling point below 230°.

The hydrogenation of oil, however, has been worked on a commercial scale. The oil is treated in a double-walled autoclave, nitrogen, at a high temperature and a pressure equal to that of the hydrogen, and oil being circulated through the outer chamber; by this method a uniform temperature condition can be maintained, while the wall of the bomb may be much less massive than would be required otherwise. The principal objections to the Bergius process in the past have been the capital cost of the plant and the length of time taken by the reaction.

The process has been investigated in considerable detail by continental experts and their views are extremely favourable. P. Erculisse²⁰ deals exhaustively with the production of liquid from solid fuels and emphasises the commercial importance of the Bergius process.

The Soc. Financière de Transports et d'Entreprises Industrielles, of Brussels, has made an exhaustive investigation into the process, and by their permission, the following data have been taken from the reports of their experts. Generally speaking, the Berginisation of a heavy oilyield 30% of light spirit, 30% of fuel oil, 30% of Drie oil, and 10% of gas. The quantity of hydrogen required is approximately 1% for heavy oils, 2% for liquid tar, 3% for coke-oven tar, and 4% for coal. The calorific value of the products is greater than that of the materials treated, despite the fact that the reactions are exothermic. This is due to the recovery to a great extent of the latent heat of the hydrogen.

The process they consider to be technically perfect, the only portion where much improvement is possible being in the cheapening of the cost of hydrogen production. As pure hydrogen is not required, they consider that the utilisation of hydrogen from coke-oven gas offers the greatest possibilities in this direction.

²⁰ *Bull. Soc. Belge Ing.*, 1923, 4, [1].

The capital cost of a plant to treat 100 tons of oil per day of 24 hours is approximately £160,000. Working costs calculated on Belgian figures are of a character which show a good profit on the capital outlay required. These figures are to a certain extent estimates, but they are submitted by independent experts of high standing, and indicate that the process, apart from its interesting theoretical character, is one of which the technical and commercial possibilities require very serious consideration.

The great disadvantage of the Bergius process lies in the high pressure and temperature and prolonged period of treatment required, and for that reason numbers of inventors have suggested the use of catalysts. Several of these were mentioned by Shatwell in his review of the subject,¹⁸ but the following additional ones may be of interest.

M. Melamid,²¹ using tin-lined vessels, claims an 80–90% conversion of heavy oil into oil of low boiling point, with a pressure of only 10–20 atmospheres and a temperature of only 250°–320° C. The tin acts as a catalyst, while tar oils or mineral oils may be used.

H. Plauson and J. A. Vielle,²² using nickel or nickel steel tubes, found that the pressure required for hydrogenation of coal varied with the temperature. Thus at 600° C. only 50–60 atm. was necessary, but at 400° about 150–200 atm. was required.

An interesting process in which the addition of hydrogen is dispensed with is being developed by G. P. Lewis.²³ In this system, which applies particularly to lignites and peat, the solid material is ground to an impalpable powder, suspended in mineral oil, and then passed through tubes at a pressure not exceeding 25 atm. and at a temperature of approximately 500° C. A Canadian lignite treated in this way gave an oil yield of 68 gallons per ton, of which 12·2 gallons was motor spirit, whilst nearly 80% boiled below 300° C. By the addition of a suitable catalyst to the mixture of coal and oil the yield of motor spirit is almost doubled.

Generally speaking, whilst large-scale plants have yet to be erected, the hydrogenation of solid fuels offers extremely important possibilities, especially in the treatment of fuel of recent formation, and in many cases give promise of being, when perfected, a valuable means of utilising deposits which are at present difficult to exploit on any extensive scale.

COAL ANALYSIS AND TESTING.

The need for a standardised system of coal analysis has been long felt, not only by scientific workers on coal but by the commercial interests involved in handling the material.

²¹ E.P. 171,367; *J.*, 1923, 218A.

²² E.P. 182,852; *J.*, 1923, 593A.

²³ E.P. 175,670; *J.*, 1922, 283A.

For this reason the recent report by the Fuel Research Board²⁴ on methods of coal analyses will be welcomed. It is to be hoped that the methods suggested will be universally adopted by British chemists in order that results from different laboratories may be standardised as much as possible.

Of growing importance in this direction is the necessity of a standard method of determining the caking index of coal. The method suggested in the report is a modification of the Campredon test, in which the weight of sand which can be bound into a coherent coke by unit weight of coal is determined. Further details of the method have been given by T. Gray,²⁵ and it is stated that results show a surprisingly close agreement with those obtained by heating ground coal in cotton bags in a coke-oven.

The uncertain factor is, of course, the sand, and different sands give different values for the caking index. In a brief review of the subject²⁶ A. Badarau and F. Tideswell have suggested the advisability of determining a "caking power curve" for each coal, from a determination of the crushing strength of a range of mixtures of coals and inert materials.

Electrode carbon, the use of which had been previously suggested by F. S. Sinnatt and A. Grounds,²⁷ was used as an inert material, and it was found in a series of tests that there were two types of coal: (1) coals of high initial coking strength which rapidly falls on addition of inert material, and (2) coals of low initial coking strength which rises on addition of inert material. The change from the first to the second type seemed to follow a decrease in the oxygen content of the coal. Other papers were read on the subject at the Congrès de Chauffage Industriel in Paris by J. St. Clair-Deville²⁸ and A. Meurice²⁹ and these emphasised the necessity for the determination of crushing strength.

The methods suggested are all of service in so far as existing methods of coke manufacture are concerned. They give an idea as to whether a coal can be carbonised in an existing coke oven to give a coke suitable for blast-furnace work, but they are all more or less empirical. The character and strength of a coke can be modified so profoundly by the preliminary treatment of the coal (grinding and briquetting) and by the method and rate or temperature of carbonisation, that considerable further work on this very interesting subject is desirable.

²⁴ "Physical and Chemical Survey of the National Coal Resources," Fuel Research Board, No. 2, H.M. Stationery Office.

²⁵ *Fuel*, 1923, 2, 42; *J.*, 1923, 341A.

²⁶ *Fuel*, 1923, 2, 61; *J.*, 1923, 537A.

²⁷ *J.*, 1920, 83T.

²⁸ *Fuel*, 1923, 2, 296.

²⁹ *Fuel*, 1923, 2, 305.

The accurate determination of the specific gravity of coal is of importance in connexion with coal washing, and the paper on this subject by T. J. Drakeley and W. O. Jones³⁰ will be welcomed by coke-oven chemists and others engaged in this branch of the industry.

Useful work has also been carried out by G. Coles³¹ on the specific heat of coal. The general character of the effects of the moisture content, volatile matter, and carbon: hydrogen ratio has been determined. The work should be of value in connexion with investigations on the spontaneous heating of coal, and to a lesser extent in investigations on thermal phenomena of coal carbonisation. (See also *Fuel*, 1923, **2**, 152, 186, 298, 317, 330, 344, 362, 373.)

CONSTITUTION OF COAL.

The vexed question of the constitution of coal has continued to receive considerable attention during the past year. In a series of papers on the spontaneous combustion of coal in relation to its composition and structure, M. C. Stopes and R. V. Wheeler³² have taken the opportunity of giving a review of modern ideas of coal constitution and particularly of the properties of the four constituents of banded bituminous coal, vitrain, durain, clarain, and fusain, and the influence of these ingredients on spontaneous combustion. Thus the high rate of oxygen absorption at comparatively low temperatures of fusain noted by Tideswell and Wheeler is mentioned, but doubt is expressed whether fusain had a preponderating influence once heating had begun, as the other constituents—especially vitrain and clarain—were more readily oxidised at a later stage. The physical structure of the various components probably accounted for the difference in absorption power.

The influence of fusain is emphasised by the work of F. S. Sinnatt and L. Slater³³ on the spread of propagation of combustion in coal. Fusain is the most friable portion of the coal, and it was found that the degree of fineness of the coal played an important part in determining the speed of propagation of combustion through the mass. Results contrary to the above views have been obtained by J. I. Graham,³⁴ the oxygen absorption observed by him with fusain at low temperatures not being nearly so great as those found by Tideswell and Wheeler, probably owing to the size of the particles adopted by the latter and partly to difference in composition of the fusain treated.

³⁰ *J.*, 1923, 163T.

³¹ *J.*, 1923, 435T.

³² *Fuel*, 1923, **2**, 29, 83, 122; *J.*, 1923, 537A.

³³ *Fuel*, 1923, **2**, 211; *J.*, 1923, 876A.

³⁴ *Colliery Guardian*, Nov. 16, 1923.

Graham found, however, that the samples of fusain examined by him absorbed oxygen at low temperatures at a lower rate than that shown by coals liable to spontaneous combustion.

In discussing this paper R. V. Wheeler³⁵ considered that the differences observed were due to the difference in the temperatures adopted. In the experiments of Tideswell and Wheeler a higher temperature was used than in those of Graham. There does seem a likelihood that fusain plays the part of the "villain of the piece," and further work on the subject is looked forward to with interest.

The extremely valuable results obtained from the palaeo-botanical examination of coal sections are now universally recognised by fuel technologists, but the preparation of these specimens requires a degree of manipulative skill which the average chemist has not, generally the time to acquire. Further difficulties have been experienced in preparing suitable sections from steam coals and anthracites. For this reason the methods suggested by H. Winter³⁶ of examining microscopically the coal by reflected light are of considerable interest. After grinding and polishing, and etching with a suitable reagent, it is possible to distinguish clearly in many cases the plant structures (pollen grains, seeds, spores, etc.) in the coal.

This matter has been quickly followed up, and C. A. Scyler³⁷ describes the result of an examination of dull and bright anthracites. The bright coal showed every appearance of spore structures similar to those of durain. Dull anthracite coal frequently contains bands showing cellular débris. Fusain is often present in anthracite and cell structure is clearly evident. The banded constituents of coal therefore persist in anthracite, and the fact will have an important bearing upon the theory of anthracitation.

Chemical methods of attacking the problems of coal constitution have been followed up by several observers. A. R. Pearson³⁸ considers coal to contain (1) resinic compounds soluble in pyridine and chloroform, and (2) condensation compounds of celluloses. He gives to these the name "ultrahumins," and classifies them into α -, β -, and γ -ultrahumins; ultrahumins which are not resinic are insoluble in pyridine; β - and γ -ultrahumins are soluble. The difficulty of removing pyridine from these extracts is well known, and, unfortunately, prolonged heating to remove pyridine destroys coking properties, which α - and β -ultrahumins possess. It has been found possible, however, to replace pyridine in the

³⁵ Iron and Coal Trades Review, Dec. 14, 1923.

³⁶ Fuel, 1923, 2, 78; J., 1923, 537A.

³⁷ Fuel, 1923, 2, 217; J., 1923, 876A.

³⁸ J., 1923, 68T.*

adsorption completes, and derivatives of definite composition have been produced in this way with sulphuric acid—called oxahumins—and from these brominated derivations have been formed. The conclusion is arrived at that the ultrahumins contain a stable molecular nucleus of which nitrogen is probably a constituent element.

F. V. Tideswell and R. V. Wheeler³⁹ have examined the doplerite found in peat beds. The material is essentially a mixture of acid anhydrides, the original lignone and cellulose groupings being preserved and new ring compounds of the pyrrole and furan series are also present. The substance is similar to the "vitrain" of bituminous coal in many respects. Somewhat similar material has been examined by W. Schneider⁴⁰ and H. Winter.⁴¹

The extremely interesting controversy that has been raging regarding the parent type of substances in a coal continues. F. Fischer and H. Schrader have elaborated into a pamphlet their reasons for the view that the parent substance in bituminous coal is lignin and not cellulose.⁴² They have continued their researches with the adoption of the following methods:—(1) Action of solvents; (2) action of alkalis; (3) pressure oxidation of peat lignites and coals in the presence and in the absence of various oxides; (4) low-temperature distillation of these materials; (5) the study of the products of decay of vegetation, cellulose, and lignin.⁴³ This work points to the existence of an essentially aromatic structure in coal which would agree with the lignin derivation theory, whereas cellulose derivatives would have a furan structure.

In a review of the work of Fischer and Schrader, D. T. Jones⁴⁴ points out that the drastic chemical methods adopted by these observers would have a tendency to modify the structure of the residual material, and that in the conditions of the experiment the aliphatic compounds would become converted into aromatic ones, so that the theory is not proved from the chemical standpoint. Another point of view is submitted by H. J. Page.⁴⁵ From the standpoint of the soil chemist he has reviewed the evidence for and against the cellulose and lignin theories, but the result of this analysis again must leave the verdict as "not proven." The work of A. Pictet on the distillation of lignin has also been briefly

³⁹ *Chem. Soc. Trans.*, 1922, **121**, 2345; *J.*, 1923, 83A.

⁴⁰ *Ges. Abhandl. Kennt. Kohle*, 1920, **5**, 541; *J.*, 1923, 130A.

⁴¹ *Glückauf*, 1922, **58**, 1533; *Fuel*, 1923, **2**, 58.

⁴² *Fuel*, 1922, **2**, 93, 133.

⁴³ *Ges. Abhandl. Kennt. Kohle*, 1920, **5**, 1, 34, 37, 46, etc.; *J.*, 1923, 3A, 4A, 130A, 131A.

⁴⁴ *Fuel*, 1923, **2**, 387.

⁴⁵ *Fuel*, 1923, **2**, 232.

reviewed by D. T. Jones,⁴⁶ and this again seems to indicate that the conclusions of Fischer and Schrader are premature.

This subject, however, is extremely fascinating, and whether cellulose⁴⁷ or lignin ultimately prove to be the parent substance of coal, a vast amount of useful knowledge is being gained which will be of service to the chemist. (See also *Fuel*, 1923, 2, 93, 95, 166, 167, 387.)

LOW-TEMPERATURE CARBONISATION.

The carbonisation of coal at low temperatures occupies a position intermediate between that of the hydrogenation or other treatment of coal for the production of liquid fuel and its treatment for the production of a high-temperature coke. In many cases, where solid fuel is cheap and liquid fuel expensive, it is economic to regard low-temperature carbonisation simply from a fuel oil standpoint, and to consider the carbonaceous residue as a by-product. In England, on the other hand, the production of a hard, smokeless, free-burning solid fuel is the primary consideration, whilst the liquid and gaseous products are merely by-products.

Low-temperature carbonisation schemes must therefore be considered from one or other of the above viewpoints, and the particular system of retorting to be adopted in any particular case might very well depend on the market conditions at the site where the scheme is adopted.

During the past year the growing literature on this subject has been added to by descriptions of a few new retorting processes, some of which present novel features, and by the extension of already existing systems.

Low-Temperature Carbonization, Ltd.,⁴⁷ announce that their Barnsley plant is to be increased to 500 tons a day capacity. They claim the following yields on a throughput of 8230 tons of coal :— Smokeless fuel, 6210 tons; tar, 172,565 gallons; gas, 38 million cubic feet of over 800 B.Th.U. per cubic foot.

A low-temperature scheme of considerable magnitude is being developed by the Henry Ford Co., at Detroit. The process used is the "Piron" system, developed by A. V. Caracristi. In this process⁴⁸ the coal is coked on a movable conveyor composed of joined metallic plates. These are heated by means of a lead bath, the temperature of which can be controlled within narrow limits. The coal is charged in very thin layers, so that the rate of carbonisation is very rapid. The solid fuel is a semi-coke which can

⁴⁶ *Fuel*, 1923, 2, 387.

⁴⁷ *Chem. and Ind.*, 1923, 1100.

⁴⁸ *Iron and Coal Trades Review*, August 24, 1923.

be easily pulverised, and it is proposed to use the bulk produced as a powdered fuel, the remainder being briquetted with a binder. A process of another type has been suggested by J. S. Morgan⁴⁹ in which the coal is passed directly on to a lead bath. It is not stated whether this has been tried out on a semi-commercial or commercial scale.

A process of somewhat novel type has been patented by H. Koppers,⁵⁰ in which the heat is imparted to the charge by means of steel balls of 100–125 mm. diameter, which have been pre-heated to a temperature of say 800° C. These are charged with the coal into a revolving drum; after they have given up their heat, the pulverised coke formed is discharged through a screen whilst the steel balls are returned to the pre-heating furnace.

In the above processes the coke is produced in powdered form, and if required as a solid fuel for domestic or industrial purposes must be briquetted.

A. Thau⁵¹ describes the Fellner and Ziegler rotary retort, which is working at Gelsenkirchen on a throughput of over 80 tons of coal per day. The large coke produced is gasified in producers, whilst the small coke is briquetted.

The production of saleable lump coke by low-temperature carbonisation in vertical retorts is dealt with by the Fuel Research Board.⁵² In a series of experiments made in continuous vertical retorts, using a mixture of 60% of caking coal and 40% of non-caking coal in the uncrushed state, a good coke consisting of large conglomerate masses was produced with the production of about 20% of breeze. When made at 770° C. the combustibility of the fuel was high enough to allow it to be used in open grates. It was found very advantageous to use steam in the process, and this decreased the proportion of breeze, increased the yields of tar, gas, and sulphate, and increased the throughput. A useful feature of the tests made consisted of determinations of the heat required for carbonisation with varying percentages of steam. The retorts used were externally heated and had a throughput varying from 1·74 to 2 tons a day. The retorts used were, of course, designed for high-temperature work, and it is suggested that cast iron or mild steel retorts would be more favourable to good working.

The best results from every standpoint (including that of thermal efficiency) were obtained when a maximum quantity of steam was used, and it might be of interest to compare the results obtained with those in a plant of somewhat smaller capacity—1 ton

⁴⁹ *Iron and Coal Trades Review*, April 13, 1923.

⁵⁰ E.P. 184,144; J., 1923, 442A.

⁵¹ *Iron and Coal Trades Review*, April 6, 1923.

⁵² Technical Paper No. 7. H.M. Stationery Office.

a day—by E. R. Sutcliffe and the writer, in which steam alone superheated to 750° C. was utilised as the heating medium, no external heating being employed.

| | Fuel Research Board test. Externally-heated retort. | Internally-heated retort. | Results in internally-heated retort calculated on raw coal basis. |
|------------------------------------|--|---|---|
| Character of coal charged. | 60% Mitchell main. 40% Ellestown main. | Briquettes of 70% Trenchbone and 30% coke breeze. | — |
| Volatile matter in coal charged .. | 32.4% | 24.4% | — |
| Percentage of steam used .. | 20% | 125% | — |
| <i>Distillation results.</i> | | | |
| Coke, % .. | 71.7% | 71.95% | — |
| Gas, cub. ft. per ton .. | 7,750 of 640 B. Th. U. | 12,560 of 437 B. Th. U. | 17,943 c. ft. |
| Tar, gall. per ton .. | 16.62 | 10.66 | 18.30 |
| Light spirit, gall. per ton .. | — | 2.64 | 4.78 |
| Sulphate, lb. per ton .. | 28.2 | 37.63 | 53.75 |
| Volatile matter in coke .. | 6.3% | 5.0% | 5.0% |
| Temperature used .. | 664° C. | 750° C. | 750° C. |

A feature of the above results is the high gas yield in an internally-heated retort at the comparatively low temperature used. To a slight extent a water-gas reaction is taking place between the steam and solid carbon, but this in itself would not account for the increased yield, and there seems a probability of interaction of steam with the volatile hydrocarbons left in the coke, facilitated by the reactivity of the coke made. Useful particulars are given by the Fuel Research Board of the distillation and washing tests of the tars made.

Very little systematic work has been done in England on low-temperature tars, but research has been actively pursued on the Continent on the character of these products. The character of the tars produced varies considerably with the character of the coal used, the retorting temperature and the type of retort used. The complex nature of this subject can be gathered from an examination of some of the continental work on the subject.

E. Fromm and H. Eckard⁵³ found that two geologically similar lignites gave two dissimilar tars in the same retort, differences existing in the neutral, basic, and acidic portions. These differences were attributed to dissimilar botanical origin.

Low-temperature tars have been obtained by F. Fischer and his collaborators, which differed very considerably from those obtained by F. Schütz and his co-workers.⁵⁴ These differences were attributed by Fischer to overheating in the case of tars tested by Schütz, but the latter worker disagrees with this suggestion and attributes the differences observed to the method of treatment of the tar adopted by Fischer. A detailed examination of these results is out of place in this brief note, but the point is mentioned in view of the ultimate importance of the subject, if and when the low-temperature or fractional distillation of coal is embarked upon on a large scale.

Generally speaking, the position with reference to low-temperature carbonisation is that whilst many processes are now being worked on a semi-commercial or small commercial scale, not one has yet attained the position of being able to publish a working balance sheet actually showing a profit on continuous working over a prolonged period, and, until that can be done, rapid extension of any process of smokeless fuel production can hardly be looked for.

The general tendency in most recent work is to carbonise at medium temperatures (700° - 750° C.) rather than to limit the temperatures to 500° or so, as suggested by earlier workers. The volatile matter in the coke produced is, of course, considerably reduced, but by due attention to the preliminary preparation of the coal and by the utilisation of suitable types of coal, the combustibility of the product is still maintained at a point which would allow of the resulting fuel being used in the domestic grate.

BLAST-FURNACE COKE.

The continued depression in the iron and steel industry has stimulated investigations into methods of reducing the fuel consumption in the manufacture of pig iron and steel. The basis of the iron and steel industry is, of course, furnace coke, and more and more emphasis is being laid on the necessity of purity and freedom from ash and sulphur in this material. The effect of these ingredients is cumulative in so far as fuel consumption in blast-furnace practice is concerned, and a high ash or high sulphur content in the coke increases the fuel consumption much more than the amount that is actually required to fuse the ash or to eliminate the

⁵³ *Ber.*, 1923, **56**, 948; *J.*, 1923, 488A.

⁵⁴ *Ber.*, 1923, **56**, 162, 601, 869; *Brennstoff-Chem.*, 1923, **4**, 49, 84; *J.*, 1923, 175A, 261A, 343A, 344A, 488A.

sulphur as the case may be. For this reason, considerable attention is now being given to methods of reducing the proportion of these ingredients in coke.

The problem of eliminating shale from finely-divided coal can now be regarded as solved, and this in itself allows of the production, without excessive loss in washing, of a product of much lower ash content than was formerly possible.

By the use of a Draper fine coal washer, one South Wales coking installation is turning out coke with a guaranteed ash content of less than 7%, which is a marked improvement on results obtained in the past.

The washing of coal fines is not an easy operation, and the difficulties involved, together with the theoretical principles, are discussed by L. Lococq.⁵⁵ Particulars of various types of coal washers are given together with a detailed description of the Rhôloâveur system.

A process of an entirely different type is that of froth flotation. This process is able to treat coal in a fine state of subdivision, but difficulties have been experienced in the past in de-watering the concentrates obtained. These, however, have now been overcome by a process⁵⁶ of flocculating the coal concentrates with tar and the like and extruding the water by a pressure of about 2 tons per square inch. According to another process,⁵⁷ economy in the use of tar is obtained by separating the most finely-divided part of the coal, flocculating this with tar, and finally mixing the flocculated fines with the coarser coal and subjecting the mixture to pressure. The process requires the use of only a small quantity of oil, but a process at the other end of the scale, the Trent process,⁵⁸ necessitates the use of a considerable proportion of oil. An interesting comparison of the two processes was given by O. C. Ralston,⁵⁹ and it is suggested that the two processes could be used to supplement one another, the froth flotation system being used with coals down to the size of "slime" and the Trent process for the latter product. The Trent process, however, suffers from the disadvantage that the oil-coal "amalgam" produced has to be distilled if the oil is to be recovered.⁶⁰

An interesting method of drying washed coal fines is that of R. F. Fabry,⁶¹ in which the coal is dried centrifugally, in a continuous machine.

These new developments in coal cleaning are of considerable promise to the iron and steel industry. They allow of the pro-

⁵⁵ *Fuel*, 1923, 2, 255.

⁵⁶ W. Broadbridge and others, E.P. 193,947; *J.*, 1923, 438A.

⁵⁷ W. W. Stenning and others, E.P. 193,466; *J.*, 1923, 392A.

⁵⁸ Cf. E.P. 151,236 and 183,430; *J.*, 1921, 684A; 1923, 392A.

⁵⁹ *Colliery Guardian*, Feb. 9, 1923.

⁶⁰ Cf. E.P. 182,006 and 202,910; *J.*, 1922, 621A; 1923, 1052A.

duction of a coke of increased purity, with a consequent decrease in the fuel consumption per ton of iron made.

Another factor of considerable importance is the sulphur content in the coke. A high-sulphur coke adds considerably to the fuel consumption in iron manufacture, and with the decreasing supplies of high-class coking coal, the trouble is already becoming acute in certain districts in this country.

The work of A. R. Powell⁶¹ on the question is extremely useful. He has found that sulphur exists in coke in three or perhaps four forms, *viz.*, ferrous sulphide, adsorbed free sulphur, sulphur in solid solution, and sulphates. Of these the ferrous sulphide is the easiest to eliminate. It is removed to some extent during the coke-quenching operation; it can be completely oxidised at 500° C., and is partly removed by the action of hydrogen on the incandescent coke. The removal of the other forms of sulphur from coke, however, is difficult, and much more promise is attached to its elimination from the coal prior to coking.

A. Lissner⁶² states that the removal of sulphur from coal is impracticable, except in the case of inorganic sulphur (pyrites etc.), which can sometimes be removed by elutriation. Organic sulphur is difficult to separate. Organic solvents have no selective action on the sulphur-bearing constituents, and only the most vigorous action by bromination or oxidation at 250°–270° C. had any effect.

The writer has found that coals differ very considerably in so far as sulphur removal is concerned. Inorganic sulphur in the form of pyrites can be separated by fine grinding and washing in a suitable apparatus, while organic sulphur can frequently be considerably reduced by fractional distillation of the coal in steam. Thus, in one case, a coal of 3% sulphur had a content of only 2% after grinding and washing, whilst this coal when heated to 800°–900° C. in a current of steam gave a coke with only 1.15% of sulphur. In another case, a Yorkshire coal carbonised in steam at 790° C. by the Sutcliffe-Evans process gave a coke containing 1.19% of sulphur as compared with 1.92% in the coal and 1.55% in a coke made from the same coal without steam. Similar procedure with other coals, however, has not given such favourable results, and a good deal depends on the type of coal treated. The problem is an important one and there is room for considerable work in it.

⁶¹ *J. Amer. Chem. Soc.*, 1923, **45**, 1; *Amer. Inst. Min. Met. Eng.*, Feb., 1923; *Gas World*, 1923, **78**, Coking Sect., 59; *Ind. Eng. Chem.*, 1923, **15**, 951; *J.*, 1923, 214A, 455A, 697A, 1009A.

⁶² *Naturprodukte*, 1923, 113; *J.*, 1923, 964A.

MANUFACTURE OF COKE.

A few features of general interest have been announced during the past 12 months. In view of the recent attention given to the preheating of coal prior to carbonisation, the announcement of the method of treating Sarre coals by a two-stage process is of peculiar interest.⁶³ In the process now adopted the coal is first heated to a temperature of 60° C., and when carbonisation is complete at this temperature the resulting soft coke is charged into ordinary coke ovens and carbonised under normal conditions of temperature. By this means a good hard coke is produced which is suitable for blast-furnace purposes.

A new type of coke-oven suitable for use in such a two-stage process has been patented by the Soc. de Fours à Coke.⁶⁴ A process of the above type appears to have considerable promise in dealing with certain types of high-volatile coals, and the pre-heating of the coal considerably improves the quality of the resulting product. A slightly different system was announced by K. Shimomura.⁶⁵ In a Japanese Patent taken out in 1908 he proposes to heat coal to a sufficient temperature to reduce the volatile content in the resulting coke to about 15%. The residue is then mixed in suitable proportions with raw coal and carbonised in the usual way. By this means the products from coals which customarily give a fingery type of coke, give a blocky coke, hard and strong enough for furnace work.

Heat balance sheets of the coking process have been drafted by D. S. Chamberlain and E. W. McGovern,⁶⁶ and by D. W. Wilson, H. V. Forrest, and C. H. Hitz, junr.⁶⁷ From a point of view of thermal efficiency the regenerative coke-oven comes out fairly well, the biggest item of loss in both cases being the sensible heat in the coke. Several attempts have been made to recover this, and the method recently proposed by Sulzer Frères⁶⁸ of cooling the coke with inert gases seems particularly promising. The heat extracted from the coke is used for steam raising. A large installation is now being erected at the Pictou Coke Ovens at Homécourt, and it is anticipated that the coke heat from a 1000-ton-a-day battery will generate 28,000 lb. of steam per hour at a pressure of 140 lb. per sq. inch. The system offers the further advantage of reducing the moisture in the furnace coke.

⁶³ *Chem. and Ind.*, 1923, 794.

⁶⁴ G.P. 366,472; *J.*, 1923, 439A.

⁶⁵ *Chem. and Ind.*, 1923, 556.

⁶⁶ *Gas World*, 1923, 79, *Coking Sect.*, 42; *J.*, 1923, 436A.

⁶⁷ *Ind. Eng. Chem.*, 1923, 15, 251; *J.*, 1923, 389A.

⁶⁸ E.P. 199,182, *J.*, 1923, 258A.

•COMBUSTIBILITY OF COKE.

Research in various directions is being actively pursued on the subject of combustibility of coke. E. R. Sutcliffe and E. C. Evans⁶⁹ deal in considerable detail with the question from a blast-furnace standpoint. They hold that a high degree of combustibility in a coke implies a high reactivity to or solubility in carbon dioxide. The latter property in a coke has been almost universally condemned by furnace managers, but these authors consider that the endothermic reaction between carbon and carbon dioxide lowers the active zone in the furnace, and concentrates the reducing reactions in the region of the greatest thermal activity. Further, a reactive fuel would have a direct action on the mixture of molten metal and oxides in the melting zone of the furnace. The oxides present would be reduced far more readily by a reactive fuel than by an inactive one, and this action, together with the "direct reduction" of the ore by reactive coke, would reduce the chemical requirements of carbon to a point which would result in a considerable saving in the fuel consumption of the furnace.

The possibilities in this direction of a combined process of direct and indirect reduction were brought out by F. Clements⁷⁰ in the discussion on the above paper. He stated that iron has been produced in an experimental plant of considerable capacity with an expenditure of only 900 lb. of bituminous coal per ton of iron made, and that this indicated considerable support for the views expressed by the authors. The revolutionary suggestions made, however, could not pass unchallenged. The most important arguments advanced against these suggestions are based upon the results of tests made under the supervision of the American Bureau of Mines. In a series of papers by R. A. Sherman, J. Blizzard, G. St. J. Perrott, and S. P. Kinney,⁷¹ comparisons of different types of coke in a gas producer and blast furnaces are made. The combustibilities of the cokes were calculated from the carbon monoxide content in the gases at various depths in the producer, and one of the conclusions arrived at was that the solubility of coke in carbon dioxide did not necessarily correspond to its reactivity to oxygen (this result differs from that obtained by R. V. Wheeler, cf. *infra*). These observers could perceive no apparent connexion between the combustibility of the coke used and the fuel consumption in a blast furnace.

The conclusions arrived at by these authors are expressed very cautiously, and this is very desirable in a subject in which so many complexities exist. Gas analyses of blast furnaces worked primarily to give the maximum output of iron may lead to misleading con-

⁶⁹ *J. Iron and Steel Inst.*, 1923, **107**, 27; *J.*, 1923, 552A.

⁷⁰ *Ibid.*, **107**, 84.

⁷¹ Amer. Inst. Min. Met. Eng.; cf. *J.*, 1923, 436A.

clusions from the point of view of the fuel technologist. Further, it is possible to draw very different interpretations from the valuable mass of data that these observers have collected according to the viewpoint from which it is regarded.

On the other hand analyses of the hearth gases can indicate very clearly the amount of work thrown upon the hearth. A high excess of combined oxygen, for example, can only result from delayed reduction of the ore, and it is significant to note that in the furnaces selected by these observers, the lowest fuel consumption was accompanied by high excess of combined oxygen in the hearth gases. This result is what would be expected from the theories of Sutcliffe and Evans. Further investigation on this important subject is, however, being continued, and it is to be hoped that the data now being accumulated will clear up a matter which is of very considerable importance to the iron and steel industry.

Considerable work has been done in laboratory investigations of "combustibility" of fuels. K. Bunte and A. Kölmel⁷² have investigated the ignition temperature of cokes. R. V. Wheeler⁷³ describes a method of determining "reactivity" by the rate of oxidation in air, and in carbon dioxide, and gives results for different types of coke, whilst further work has been done by A. Korevaar,⁷⁴ K. Bunte,⁷⁵ P. K. Breuer and A. Broche,⁷⁶ F. Heyd,⁷⁷ and F. Schreiber.⁷⁸ Generally speaking, the results obtained are in conformity with the views of E. R. Sutcliffe and E. C. Evans,⁷⁹ and of G. T. Beilby,⁸⁰ that the combustibility of a coke is a function of its structure. Heyd, however, considers that the inorganic constituents of the coke play a part in determining its combustibility. This view has been controverted by some observers, but in view of the differences in catalytic power possessed by different inorganic materials, there seems no reason why the composition of the ash should not exert an influence. Some force is given to the hypothesis by the fact that the nature of the ash plays an important part in determining the "activity" of a charcoal with respect to its power of gas absorption.⁸¹ As this property is due essentially to the character of the surface, it seems quite possible that the character and content of the ash in coke would influence its combustibility.

⁷² *Gas u. Wasserfach*, 1922, **65**, 592; *J.*, 1923, 132A.

⁷³ *J. Iron and Steel Inst.*, 1923, **107**, 75.

⁷⁴ *Stahl u. Eisen*, 1923, **43**, 431; *J.*, 1923, 388A.

⁷⁵ *Brennstoff-Chem.*, 1923, **4**, 167; *J.*, 1923, 697A.

⁷⁶ *Ibid.*, 168; *J.*, 1923, 697A.

⁷⁷ *Ibid.*, 198; *J.*, 1923, 813A.

⁷⁸ *Ibid.*, 273; *J.*, 1923, 1009A.

⁷⁹ *J.*, 1922, 196T.

⁸⁰ *J.*, 1922, 341T.

⁸¹ O. Ruff and others, *Kolloid-Zeits.*, 1923, **32**, 225; *J.*, 1923, 644A

GAS—DESTRUCTIVE DISTILLATION— TAR PRODUCTS.

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THE year under review has been characterised not by epoch-making changes in process or principle, but by an unusually large number of papers embodying the results of careful work directed towards obtaining a maximum of efficiency and a reduction of operating costs. It is pleasant to record the growing appreciation of the value of expert chemists in the gas and coke-oven industries, and minor gas works are already exploring the possibilities of co-operative chemical supervision.¹ Such a venture, should it be fruitful, could only result in the good of all concerned—the public, the industry, and the chemical profession.

The elasticity conferred by the Regulation Act of 1920 has occasioned critical examination of the possibilities of employing heating gas of widely varying thermal values (200–750 B.Th.U.) as stages in the manufacture of the most economic fuel for distribution and consumption, and increased attention has been paid to domestic and industrial burning appliances. Criticism, much of which was ill-informed, has been directed against the thermal basis of charging for gas supply; this was the subject of investigation by a Departmental Committee of the Board of Trade,² which unanimously reported in favour of the therm and of its extension to all statutory gas undertakings within the scope of the Act. A like criticism, not altogether disinterested, has attacked the carbon monoxide content of town's gas,³ the chief result of which has been only to consolidate present practice.

COMBUSTION.

Slow oxidation of hydrocarbons forms the subject of an extended series of investigations by T. S. Wheeler and E. W. Blair.⁴ Briefly, the results indicate that (1) in the case of ethylene mixed with ozone, an ozonide is first formed which subsequently decomposes

¹ *Gas World*, 1923, **78**, 367.

² *Annu. Repts.*, 1922, **7**, 40; also *Gas J.*, 1923, March 17; *Gas World*, 1923, **78**, 238.

³ *Gas J.*, 1921, **155**, 429.

⁴ *J.*, 1923, **81**, 87, 260, 263, 343, 347, 415, 492T.

to formaldehyde and formic acid, hydrogen peroxide also being produced in presence of moisture; (2) for methane and oxygen, the formaldehyde production varies inversely as the temperature and time of heating; no methyl alcohol was detected; (3) the rate of oxidation of the hydrocarbon is not greatly affected by the presence of intermediate products, though catalytic agents and varied surfaces can modify it considerably; and (4) slow oxidation of hexane produces higher aldehydes, unsaturated hydrocarbons, formaldehyde, acids, carbon monoxide and dioxide, hydrogen at higher temperatures, and water. The reactions of a mixture of methane and air at 500°–900° are discussed by E. Berl and H. Fischer⁵; all observers seem to find that ammonia does not assist materially in stabilising any formaldehyde produced, though it does seem to exert a stabilising effect on formic acid.⁶

Methods of measurement of flame velocity are discussed by W. Mason,⁷ who gives details of methods developed at the Mines Departmental Experimental Station. The law of speeds in the propagation of flame is discussed by W. Payman,⁸ and the explosive wave in a mixture of carbon bisulphide and oxygen has been investigated by P. Lafitte.⁹ Experiments by W. Payman and R. V. Wheeler¹⁰ on the explosion of carbon monoxide and hydrogen with air have afforded results in accordance with the hypothesis originally put forward by Dixon concerning the function of water in this reaction. The effect of the presence of nitrogen on the reaction between carbon monoxide and air has also been studied; apparently it cannot be regarded as an inert diluent.¹¹ The explosion of a mixture of carbon monoxide, hydrogen, and oxygen is discussed by H. B. Dixon and N. S. Walls,¹² who find that when the products of incomplete combustion cool down under such conditions that no steam is condensed, the water-gas equilibrium is nearly constant. New experiments concerning the combustion of a mixture of carbon monoxide and oxygen are described by W. A. Bone.¹³ The effect of pressure on the limits of inflammability of mixtures of hydrocarbon and air is dealt with by

⁵ *Z. angew. Chem.*, 1923, **36**, 297; *J.*, 1923, 698A.

⁶ *Ibid.*

⁷ *Chem. Soc. Trans.*, 1923, **123**, 210; *Fuel*, 1923, **2**, 110; *J.*, 1923, 436A, 538A.

⁸ *Chem. Soc. Trans.*, 1923, **123**, 412; W. Payman and N. S. Walls, *ibid.*, 1923, **123**, 420; *J.*, 1923, 436A, 437A.

⁹ *Comptes rend.*, 1923, **176**, 1392; **177**, 178; *J.*, 1923, 640A, 814A.

¹⁰ *Chem. Soc. Trans.*, 1923, **123**, 1251; *J.*, 1923, 757A.

¹¹ W. A. Bone, D. M. Newitt, and D. T. A. Townend, *Roy. Soc. Proc.*, 1923, **A 103**, 205. Cf. *Chem. Soc. Trans.*, 1923, **123**, 2008; *Gas World*, 1923, **78**, 439; *Gas J.*, 1923, **163**, 415, 475; *J.*, 1923, 590A, 964A. F. Häusser, *Chem. and Ind.*, 1923, 750.

¹² *Chem. Soc. Trans.*, 1923, **123**, 1025; *J.*, 1923, 756A.

¹³ *Gas J.*, 1923, **163**, 363 et seq.

W. Payman and R. V. Wheeler,¹⁴ who find that for methane the limits of downward propagation of flame at atmospheric pressure are 6·0 and 13%, whilst at 6 atmospheres' pressure the figures obtained are 6·4 and 16%.

An interesting lecture was delivered by W. A. Bone¹⁵ to the Royal Society of Arts on surface combustion, summarising the conclusions arrived at from the beginnings of the research in 1902. A useful *résumé* of information concerning the composition of gaseous fuels in relation to their utilisation is also given by W. Payman and R. V. Wheeler.¹⁶

The determination of acetylene and ammonia formed during incomplete combustion of organic bases, e.g., aniline, carbazole, pyridine, etc., is described by K. A. Hofmann and E. Will.¹⁷ A graphic method for calculating the maximum temperatures attained during a gaseous combustion is given by F. Pollitzer,¹⁸ and O. I. Hansen and K. E. Nielsen¹⁹ deal with a method and apparatus (a modified "Orsat") for determining loss of heat in flue gases, consequent on incomplete combustion. The propagation of combustion in cones of pulverised coal is discussed by F. S. Sinnatt and L. Slater.²⁰

Aeration and air-injection of gas for burners is the subject of the Ninth Report²¹ of the Research Sub-Committee appointed by the Gas Investigation Committee of the Institution of Gas Engineers. Directly bearing upon this problem is a paper by J. S. G. Thomas and E. V. Evans²² on the entrainment of air by a jet of gas issuing from a small orifice; a standard formula that the authors deduce is claimed to be in good agreement with the experimental results.

Adjustments to burners, according to the thermal value of the gas employed, is discussed in a valuable practical paper issued by the United States Bureau of Standards,²³ and G. F. Moulton²⁴ from measurements of flame and cone heights, and analyses of the products of combustion, concludes that gases of 400–600 B.Th.U. per cub. ft. will yield the same domestic service when the appliances are correctly adjusted. Lastly an improved gas combustion furnace,

¹⁴ *Chem. Soc. Trans.*, 1923, **123**, 426; *J.*, 1923, 437A.

¹⁵ *Gas World*, 1923, **78**, 405.

¹⁶ *Fuel*, 1922, **1**, 185; *J.*, 1923, 42A.

¹⁷ *Ber.*, 1922, **55**, 3228; *J.*, 1922, 928A.

¹⁸ *Z. angew. Chem.*, 1922, **35**, 683; *J.*, 1923, 42A.

¹⁹ *Fuel*, 1923, **2**, 115; *J.*, 1923, 538A.

²⁰ *Fuel*, 1923, **2**, 211; *J.*, 1923, 876A.

²¹ *Gas World*, 1923, **78**, 589.

²² *Publ. Mag.*, 1923, **46**, 785; *J.*, 1923, 1166A.

²³ U.S. Bur. of Standards, *Technol. Paper No. 222*, 1922, **17**, 15; *J.*, 1923, 257A.

²⁴ *Ind. Eng. Chem.*, 1923, **15**, 583; *J.*, 1923, 705A.

which it is claimed is considerably superior to that ordinarily used in chemical analysis, is described by T. J. Hedley.²⁵

PEAT, LIGNITE, COAL, ETC.

Comparative figures are given by F. Fischer and H. Schrader²⁶ for the low-temperature tars obtained by dry distillation of lignin and cellulose: the yields of gas in the two cases were almost equal, the characters of the tars being somewhat different. Lignin tars and the relationship of lignin to coal are also discussed by A. Pietet and M. Gaulis²⁷: the facts elicited by these authors lend support to the theory that coal is derived from lignin.

The drying and coking of peat is described by J. Steinert,²⁸ who finds that 10–13% of tar is obtained, which included amongst other products 15% of paraffin wax and 41% of phenols. Dopplerite forms the subject of a paper by F. V. Tideswell and R. V. Wheeler,²⁹ who discuss its constitution, mode of formation, relationship to coal and the products of its decomposition at temperatures up to 600° C. The action on peat of aqueous alkalis, milk of lime, and various solvents is discussed by W. Schneider and Schellenberg,³⁰ and the pressure oxidation of peat in presence of 2.5 N alkali at 700° C. by F. Fischer and W. Schneider.³¹ Humic acids,³² their separation, properties, and reactions with nitric acid³³ and chlorine³⁴ are dealt with by Eller and his collaborators. It is well to remember in this connexion that the term "humic acids" is exceedingly generic, for the natural products, and those derived by the oxidation of phenols and carbohydrates present certain differences, the significance of which is still undetermined.

A number of papers has been contributed by F. Fischer and his collaborators³⁵ concerning the pressure-oxidation of lignites, in presence of different alkalis. Various aromatic acids were found in the products, from which it is concluded that there exists an essentially aromatic structure in coal. The pressure varied from 45 to 60 atmospheres, and the temperatures from 200° to 400° C.

²⁶ *J.*, 1923, 4322.

²⁷ *Chem. Zentr.*, 1922, **93**, III., 1184; *J.*, 1923, 136A.

²⁸ *Helv. Chim. Acta*, 1923, **6**, 627; *J.*, 1923, 755A.

²⁹ *Z. angew. Chem.*, 1922, **35**, 553; *J.*, 1923, 42A.

³⁰ *Chem. Soc. Trans.*, 1922, **121**, 2345; *J.*, 1923, 83A.

³¹ *Chem. Zentr.*, 1922, **93**, IV., 1067, 1043, 1044; *J.*, 1923, 4A, 131A.

³² *Chem. Zentr.*, 1922, **93**, IV., 1063; *J.*, 1923, 130A.

³³ W. Eller, *Annalen.*, 1923, **431**, 133; *J.*, 1923, 573A.

³⁴ W. Eller, H. Meyer, and H. Saenger, *Annalen.*, 1923, **431**, 162; *J.*, 1923, 573A.

³⁵ W. Eller, E. Herdöckerhoff, and H. Saenger, *Annalen*, 1923, **431**, 177; *J.*, 1923, 573A.

³⁶ *Ges. Abhandl. Kennt. Kohle*, 1920, **5**, 160, 186, 267, 292, 360, 366, 369, 372; *1921*, **5**, 200, 235, 319.

Dehydration of lignite for briquetting purposes etc., by heating under pressure, is patented by F. Bergius.³⁶ The same subject has also been dealt with by W. A. Bone,³⁷ who has extended his inquiries to the thermal decomposition and carbonisation of lignites.

CARBONISATION IN HORIZONTAL AND VERTICAL RETORTS.

Comparatively little attention has been paid to the horizontal retort in the literature, but steady improvement is to be noted in practice. Efficiency considerations have led to the extended use of silica retort settings,³⁸ to the full charging of the retorts, regulation of combustion chamber temperature, and to the control of retort pressure,³⁹ so that the “bogey” yield figure of 70 therms as gas is now frequently exceeded. Improvements in charging and discharging machinery are also recorded.⁴⁰

The results of an investigation of great interest in view of its bearing upon the suggestions of J. W. Cobb and H. J. Hodson⁴¹ are embodied in an excellent paper by T. C. Finlayson,⁴² who has conducted a thorough research into known and proposed processes for producing industrial oxygen, the controlling factors laid down at the outset being the necessity for low capital expenditure, and a maximum production cost of 1s. per 1000 cub. ft. The allowable cost is calculated from an assumed 90% thermal efficiency in water-gas practice, using an oxygen-enriched blast.⁴³ A critical survey of the literature of the subject, and research into new methods lead the author to conclude that chemical processes are not promising, mainly on account of thermal inefficiency. A low-temperature process involving absorption of oxygen by haemoglobin⁴⁴ was developed, but was found to be impracticable on the large scale. Physical methods involving the processes of liquefaction, followed by fractional distillation, solid adsorption, diffusion, or solubility proved to be more hopeful, but none yielded oxygen at a sufficiently low cost: a pressure fractionation process for 40% oxygen most nearly approached an economic proposition. As a subsidiary issue, the results of carbonisation, using air enriched with various amounts of oxygen, are considered, and it is shown that the efficiency of raising the calorific value does not coincide with the work done in nitrogen

³⁶ G.P. 362,074; *J.*, 1923, 258A.

³⁷ *J. Roy. Soc. Arts*, 1923, 71, 172, 189, 208; *J.*, 1923, 255A.

³⁸ G. H. Gill, *Gas J.*, 1923, 164, 409.

³⁹ W. H. Warren, *Gas World*, 1923, 78, 183.

⁴⁰ *Gas J.*, 1923, 162, 273. E.P. 206,367.

⁴¹ *J.*, 1920, 508A; *Gas J.*, 1921, 153, 806; 154, 374.

⁴² *Inst. Chem. Eng.*, June 8, 1923; *J.*, 1923, 716A.

⁴³ Cf. W. Dyrssen, *Gas J.*, 1923, 163, 940.

⁴⁴ Woodall, Duckham, & Jones, Ltd., and J. S. Morgan, E.P. 192,944; *J.*, 1923, 354A.

removal; that is, there will be a limit beyond which it will not pay to enrich the air.

The Fuel Research Board has continued the investigations of carbonisation in vertical retorts with admission of steam.⁴⁵ Using Wigan Arley coal with a combustion chamber temperature of 1180° C., the heat required to carbonise the coal and remove the products at working temperatures was 13·0 therms per ton of coal when using 5% by weight of steam, and 18·25 therms when using 20% of steam. The following yields were obtained per ton of coal:—(a)—5% of steam: Gas (502 B.Th.U. per cub. ft.) equivalent to 80·2 therms; tar, 13·62 gallons; and ammonium sulphate, 23·43 lb. (b)—20% of steam: Gas (457 B.Th.U. per cub. ft.) 91·3 therms; tar, 14·73 gallons; and ammonium sulphate 28·57 lb. (*cf.* also page 58).

A number of practical papers on the working and running costs of vertical retorts have been read during the year, of which perhaps the most interesting is that by W. Buckley⁴⁶ which, together with the discussion thereon, should be studied in the original by those interested. The 'well-kept works' records show the average yield figures for a six months' period to be 82·1 therms per ton of coal, obtained as 97,358 cub. ft. of 478 B.Th.U. gas, with coke available for sale 8·1 cwt., tar 16·45 gallons, and 10-oz. liquor 34·95 gallons.

O. Peischer⁴⁷ discusses the heat conditions of carbonisation in the Glatz type vertical chamber oven, in which the oven is heated alternately from the top and bottom, and effective regenerators employed.

E. Crowther⁴⁸ analyses the heat flow in gas carbonisation, and to improve the thermal efficiency factor revives the suggestion to return to the producer some of the waste gases direct from the flues, together with a small amount of preheated primary air, but he does not deal with the mechanical means required to effect the suggested procedure, under controlled conditions.

COMPLETE CARBONISATION; PRODUCER AND WATER GAS.

A Parker,⁴⁹ utilising the results of the researches on the continuous vertical retort given in the Fourth Report of the Institution of Gas Engineers, and on the manufacture of blue water-gas (*ibid.*, Sixth Report), and aided by certain proximate assumptions, has constructed thermal balance sheets which indicate that the single-stage process is unlikely to produce as high

⁴⁵ Fuel Research Board Tech. Paper No. 8; *J.*, 1923, 1163A; *cf. Ann. Repts.*, 1921, 6, 57.

⁴⁶ *Gas J.*, 1923, 162, 404, 414; 164, 319 *et seq.*

⁴⁷ *Gas u. Wasserfach*, 1923, 68, 565, 578; *J.*, 1923, 1058A.

⁴⁸ *Gas World*, 1923, 79, 397.

⁴⁹ *J.*, 1923, 111T. *Gas J.*, 1923, 162, 14.

a thermal efficiency as when complete gasification is conducted in two stages. The efficiency difference is small, and waste heat recovery is not considered; hence the calculations are not conclusive. Employing American coals, A. W. Warner⁵⁰ concludes that economy is best effected by expelling the volatile matter from coal at a temperature not exceeding 800° C., and at the same time removing the condensable vapours at temperatures below 400°.

Further patents covering details of the Tully plant have been granted.⁵¹ The improvements claimed include the use of a longer retort with a shallower fuel bed, a revision of the gas flow scheme, the addition of a carburettor to permit of the use of oil for enrichment, and complete gasification of the condensable hydrocarbons. Working results for this plant have been given by N. S. Smith⁵² and F. Fawcett.⁵³ The method lends itself to the production of a gas rich in hydrogen,⁵⁴ and suitable for a number of chemical processes, but on thermal and other grounds the modification is not applicable to town's gas practice, even if the carbon monoxide controversy could be maintained.

A number of patents for the preparation of methane from water-gas have been published. In three of these,⁵⁵ nickel is the catalyst employed, and incandescent molybdenum or tungsten in a fourth.⁵⁶ F. Fischer and H. Tropsch⁵⁷ have experimented with iron, employing high pressures. It should be superfluous to state that although methane has a high calorific value, yet this reaction involves a large thermal loss—1280 B.Th.U. in the form of carbon monoxide and hydrogen becoming 1000 B.Th.U. in the form of methane.

Further forms of dual generators, each retort operating alternately as a producer and as a distillation chamber, have been described.^{58, 59}

M. W. Travers and F. W. Clark⁶⁰ give detailed calculations to show that when coal is completely gasified in a generator divided

⁵⁰ Amer. Gas Assoc., Oct., 1923; *Gas World*, 1923, **70**, 44; *J.*, 1923, 877A.

⁵¹ C. B. Tully, E.P. 192,743; *J.*, 1923, 342A. E.P. 192,880, 195,798, 188,434; *J.*, 1923, 45A.

⁵² *Gas J.*, 1922, **160**, 736; *J.*, 1923, 84A.

⁵³ *Ibid.*, 1923, **162**, 26; cf. *ibid.*, **161**, 446.

⁵⁴ Ann. Repts., 1922, **6**; E.P. 195,798; *J.*, 1923, 540A. Cf. also G. Claude, *Comptes rend.*, 1923, **176**, 394; *J.*, 1923, 266A.

⁵⁵ E.P. 196,023. Cf. Armstrong and Hilditch, *J.*, 1923, 482A, 540A; also *Proc. Roy. Soc.*, 1923, **A103**, 25. G.P. 362,462 and 366,791; *J.*, 1923, 259A, 592A, 814A.

⁵⁶ Moister, Lucius, und Brüning, E.P. 186,899; *J.*, 1923, 817A.

⁵⁷ *Braunstoff-Chem.*, 1923, **4**, 193, 199; *J.*, 1923, 813A, 814A; cf. also J. S. G. Thomas, *Nature*, 1923, **111**, 778.

⁵⁸ J. R. Duff, E.P. 191,255; *J.*, 1923, 215A.

⁵⁹ E. Berg, E.P. 204,909; *J.*, 1923, 1164A.

⁶⁰ *Gas J.*, 1923, **164**, 34, 130; *J.*, 1923, 1163A.

into an upper carbonisation zone and a lower water-gas zone, the blow gases being withdrawn from a point between the two zones, the carbonisation of the coal requires two to three times the quantity of heat available in the water-gas. From this consideration they have put into operation at Aylesbury a system⁶¹ in which the additional heat required is supplied by re-circulating the mixed gas (previously partially purified) through the upper zone with the water-gas after passage through a regenerator previously heated by the blow gases. Secondary air is added to the blow gases in the regenerator, so that part of the heat of the fuel gasified during the blow is recovered. It is claimed that a yield of gas of calorific value 371.5 B.Th.U. per cub. ft., and equivalent to 184 thermjs per ton of coal, is obtained.

F. D. Marshall and R. W. Easton⁶² employ the dual system, by which the run gases from the water-gas generator pass up through the coal charge in the superposed low-temperature retort, the blow gases being ignited in the chequerwork flues surrounding the retort. The apparatus is of the dual type, in which the supply of coke to the generator is capable of adjustment to the quality of gas required, the excess being withdrawn for use for steam raising or for sale as a low-temperature fuel containing 7-12% of volatile matter. In the vertical retort two specially constructed screws are employed which propel the coal in a quiescent state. Comparative calculations for capital and working costs are given.

The results of an exhaustive enquiry into producer practice in British steel works are given by F. Clements.⁶³ The relative merits of mechanical and non-mechanical types of plant are examined; details of the cost of gasifying 1000 tons of coal per week are given; in the former type the overall figure is £103 15s., as against £112 14s. in the latter. Chemical and thermal balance sheets for different depths of fuel are provided, as is also the result of varying the saturation temperature of the blast. Attention is directed to the effect of tar and dust on the calorific value of the hot gas, which is placed at 10% over that of the cold clean gas. For high efficiency under steelworks' conditions, a high carbon monoxide content of the gas is sought, this yielding a flame of high radiating value, though mention is made of a furnace design by which more advantage is taken of the actual contact of the burning gases with the metal.

Recent developments in gas producers are reviewed by T. R. Wollaston and A. L. Booth,⁶⁴ who describe a new plant consisting of

⁶¹ E.P. 198,777; *J.*, 1923, 759A.

⁶² *Gas J.*, 1923, 162, 667.

⁶³ *J. Iron and Steel Inst.*, 1923, 107, 98; *J.*, 1923, 552A; cf. also W. B. Chapman, *Chem. and Met. Eng.*, 1923, 29, 270.

⁶⁴ *J.*, 1923, 200T.

a water-bottom type producer, upon which is superposed a mechanically-agitated retort in which the fuel undergoes partial coking by the sensible heat of the gas leaving the producer at a temperature averaging 500° C. The coked fuel is then symmetrically distributed direct to the producer, which has no refractory lining, and is surrounded by an annular jacket which may serve for steam-raising or water-heating. It is claimed that a substantially dust-free gas of gross calorific value *circa* 175 B.Th.U. per cub. ft. (45% combustibles) is obtained with a nett thermal efficiency of nearly 81%. The conditions are such as to give good yields of ammonium sulphate and of low-temperature tar. In the plant described by W. Beswick and N. E. Rambush,⁶⁵ gas of similar quality and by-products in good yield are obtained by passing the gases generated in the lower part of the producer through a column of descending fuel of such a height that practically complete low-temperature carbonisation of the fuel is effected, with simultaneous cooling of the gas, and a long time factor between steam and carbon is attained. The system involves feeding the fuel through a bell, with its mouth situated at, or slightly below, the normal level of the surface of the fuel bed, and the gas off-take springs from this bell.

The conditions required for the satisfactory gasification of lignite in producers are detailed by C. Engelhard,⁶⁶ and a suitable producer is described, together with a record of the results obtained.

The investigation of the thermal efficiency of water-gas manufacture has received continued attention. A. Parker has usefully summarised the past work of the Gas Investigation Committee of the Institution of Gas Engineers.⁶⁷ Continuing this work, the Committee has studied the effects of varying fuel bed depths, and attempts have been made to determine the relative merits of water-gas plants when operated on the Dellwik-Fleischer and Lowe-Humphreys systems.^{67A} The report is replete with a wealth of detail, and the principal results are summarised in the following table :—

| Test. | Results of Complete Tests. | | | | | Report. |
|------------------------------------|----------------------------|---------|---------|---------|---------|---------|
| | A. | B. | C. | D. | Sixth | |
| Full depth in ft. | .. | 4 | 4.25 | 5 | 6 | 7 |
| Thermal efficiencies, %— | | | | | | |
| Fuel for steam included | .. | 41.5 | 37.2 | 46.0 | 48.6 | 46.3 |
| Fuel for steam <i>not</i> included | .. | 55.0 | 51.9 | 57.5 | 60.4 | 55.8 |
| Carbon dioxide in blow gas, % | 13.0 | 16.2 | 11.8 | 12.1 | 12.2 | |
| Ratio O ₂ /CO .. | .. | 1.18 | 2.62 | 0.79 | 0.88 | 0.95 |
| Carbon dioxide in water gas, % | 4.7 | 8.2 | 5.5 | 4.5 | 4.2 | |
| Carbon monoxide in blow gas, % | 11.5 | 6.2 | 15.0 | 13.8 | 12.8 | |
| Gas made per day, c. ft. | .. | 364,400 | 307,700 | 564,900 | 614,400 | 564,200 |

⁶⁵ E.P. 188,607; *J.*, 1923, 45A; cf. *Gas J.*, 1923, 161, 141.

⁶⁶ *Z. angew. Chem.*, 1923, 36, 98; *J.*, 1923, 256A; cf. also A. Faber, *ibid.*, 1923, 36, 336; *J.*, 1923, 776A.

⁶⁷ *J.*, 1923, 111T.

^{67A} Inst. Gas. Eng., 1923; *J.*, 1923, 755A.

The loss of potential heat in the blow gas was reduced from 20%, as noted in the Sixth Report, to 11.5% in Test B, but there were increased losses due to undecomposed steam, and the output of the plant was decreased.

Calculations show that a waste heat boiler would have raised the total steam required except in two cases; in these two tests with the assistance of a waste heat boiler, efficiencies of 52.9 and 45.3% respectively were obtained. The same problem has been attacked by the Fuel Research Board⁶⁸; by varying the cycle and steam supply with a 4-ft. bed, an overall efficiency of 52.8% was obtained. J. Hall⁶⁹ has published a full record of working results, and of an efficiency test at the Temple Works, Glasgow, and has included interesting costs calculations; the data given by J. S. Thorman,⁷⁰ who describes the Kirke waste-heat boiler installation newly added to the Glover-West retorts at Stratford, should also be carefully examined. With reference to waste heat recovery in general, the present writers may perhaps be allowed to agree with the engineer who remarked that zeal for waste heat recovery must not be allowed to divert attention from the main principle—the effective use of heat units in the retort setting itself. In this connexion, E. Crowther⁷¹ suggests using the waste heat of the blow gas to preheat the blow air instead of waste heat recovery in a steam raising unit. F. Steding,⁷² working with a Dellwik-Fleischer unit, suggests jacketing the generator with a steam boiler and superheater in the case of small installations, and for larger units superposing on the generator a chequered brick-work chamber which stores heat during the blow to be utilised for vaporising water sprayed from above during the down run. R. Geipert⁷³ has studied, *inter alia*, the effect of steam current velocity on gas production and efficiency, and also the effect of the make period on the latter.

The use of bituminous coking coals as water-gas generator fuels is discussed and conditions necessary for efficient operation are detailed.⁷⁴ Attention may also be directed to the following papers of general interest:—“Heat transmission in coolers,”⁷⁵ “Chequer brickwork,”⁷⁶ “Mechanical methods for the propulsion

⁶⁸ J. G. King and J. F. Shaw, *Tech. Paper No. 6, Fuel Research Board*, 1923; *J.*, 1923, 698A.

⁶⁹ *Gas J.*, 1923, **161**, 209; *J.*, 1923, 214A.

⁷⁰ *Ibid.*, 1923, **164**, 577.

⁷¹ *Gas World*, 1923, **79**, 397.

⁷² *Gas u. Wasserfach*, 1922, **65**, 716; *J.*, 1923, 133A.

⁷³ *Ibid.*, 1922, **65**, 441; *J.*, 1923, 390A.

⁷⁴ *Tech. Paper No. 274, U.S. Bur. of Mines*; cf. *Ind. Eng. Chem.*, 1923, **15**, 355; *J.*, 1923, 482A.

⁷⁵ B. Hoastie, *J.*, 1923, 443T.

⁷⁶ U. A. Hougen and D. H. Edwards, *Chem. and Met. Eng.*, 1923, **29**, 800.

of gases,⁷⁷ also to an excellent paper by D. Lacey on "The flow of gas in pipes"⁷⁸ and a new volume entitled "Modern Gas Producers," by N. E. Rambush.

LOW-TEMPERATURE CARBONISATION.

With the growing recognition of the limitations of low-temperature carbonising processes there has been a tendency to consider their material and economic advantages when worked in conjunction with present-day methods of fuel utilisation, and more particularly in connexion with complete carbonisation plants.

- The Glasgow Corporation⁷⁹ after full enquiry has decided to erect units on the MacLaurin⁸⁰ system. In America the Piron and Illingworth processes are stated to be under investigation; the difficulties that have arisen during the development of the Carbocoal process in that country and a description of an improved form of retort, form the subject of a contribution by H. A. Curtis, W. G. Chapman, and W. G. Geldard.⁸¹
- A number of patents for retorts have been published, many of them covering modifications in detail of known types.⁸² T. M. Davidson and R. H. Abbott⁸³ apply compression to the charge while in a plastic state in the low-temperature zone (300° – 400° C.) and before it enters, as a coherent annular mass surrounding a central gas and vapour outlet pipe, a zone at a higher temperature (650° – 750°) and a third air-cooled section leading to the discharge hopper. In a later patent,⁸⁴ the same type of process is conducted in a vertical or inclined retort wherin the surfaces or portions of the surfaces of the retort in contact with the coal are given a reciprocatory movement to enable the coal to travel freely down the retort and settle compactly. The upper portion of the retort is constructed of iron, whilst lower down a refractory material is employed. W. E. Trent⁸⁵ enters a claim for a retort in the form of a Herreshoff furnace with hollow iron hearths through which the heating medium passes. S. R. Illingworth⁸⁶ patents a form of plant for the preliminary treatment described in his previous patents. Attention may also be directed to some of the processes

⁷⁷ E. F. Hooper and B. B. Waller, *J.*, 1923, 180T.

⁷⁸ Inst. Gas Eng., 1923; *Gas World*, 1923, **78**, 599.

⁷⁹ *Gas World*, 1923, **79**, 186, 272.

⁸⁰ *J.*, 1917, 620; *Iron and Coal Trades Review*, 1921, June 20, p. 848, and Nov. 11, p. 688.

⁸¹ *Chem. and Met. Eng.*, 1923, **28**, 11, 60, 171; *J.*, 1923, 132A, 191A.

⁸² E.P. 174,069, 190,819, 192,515.

⁸³ E.P. 195,711, 197,712; *J.*, 1923, 542A. E.P. 205,268; *J.*, 1923, 1214A.

⁸⁴ E.P. 206,178; *Abs.*, 1924, B, 8.

⁸⁵ E.P. 174,336; *J.*, 1923, 486A.

⁸⁶ E.P. 206,542; *Abs.*, 1924, B, 45; cf. also E.P. 175,868, 186,384, 186,085, 197,328; *J.*, 1922, 283A.

considered under the section on complete carbonisation; the Marshall-Easton process,⁷³ for example, readily lends itself to a part production of low-temperature fuel.

The Fuel Research Board⁸⁷ has designed and erected at the Greenwich Station a vertical retort for the low-temperature carbonisation of briquettes produced by the Sutcliffe-Evans system.⁸⁸ The disintegrated mixture of coals is heated to 350° C., briquetted in rotary presses, and then charged into the retorts, the open character of the charge permitting free transmission of heat throughout the mass. The experimental setting consists of four vertical retorts (15 ft. high) constructed in special cast iron and of flattened oval shape; discharge is by means of an ordinary Glover-West extractor gear. The top dimensions are 2 ft. 4 in. by 9 in., and the bottom 2 ft. 9 in. by 1 ft. 3 in. The carbonising temperature employed is 600° C.; unfortunately, experimental results are not yet available. To obtain data for the design of these special retorts, preliminary experiments were conducted in a Glover-West installation,⁸⁹ a mixture of 60% of gas coal with 40% of flame non-caking coal being employed to give a solid product containing 6.3–7.2% of volatile matter. The temperatures maintained were approximately 850° C. near the top of the retort and 700° at the bottom; steaming was found to assist the attainment of the maximum temperature, but its economic effect was not considered. Yield figures for solid, liquid, and gaseous products under these conditions are given.

COKE AND COKE OVENS.

There have been but few large extensions of coke oven plants in this country during the past five years, and probably the development which is attracting most attention is the erection by two firms of coke ovens to the full American design to which reference was made in last year's Report. The 60-oven installation at Consett⁹⁰ is to come into operation in the spring of 1924, and a considered statement after an extended run showing how far the increased capital outlay is justified by increased output with English coals, British labour, and other service charges will be awaited with considerable interest. The capacity of these ovens is 10.5 tons of dry coal and the carbonising period about 17.5 hours, equivalent to 14.4 tons per oven per day. Silica ovens of increased dimensions are now contemplated, the length, height, and mean width being 40 ft., 11 ft. 8 in., and 16 in. respectively; the charge is 11.5 tons. These ovens are designed to have a carbonising period of 16 hours, equivalent to 17.2 tons of coal treated per day. It is worthy of note

⁷³ *Gas J.*, 1923, **164**, 184.

⁸⁸ *J.*, 1922, 196T, 492A; E.P. 171,152; *J.*, 1922, 6A.

⁸⁹ *Tech. Papers No. 7*, 1923; *J.*, 1923, 917A.

⁹⁰ *Gas World*, 1923, **79**, *Coking Sect.*, 103.

that there is said to be a tendency in America to revert to fireclay walls, a still narrower oven being adopted on the ground that the temperature necessary is reduced in greater proportion and the more uniform heating yields an improvement in the by-products account.

Many attempts have been made to attain more uniform heating, including dilution of the rich fuel gas, tapering the coking chamber for the upper half, and by a change from a division of the heating pillars into flues by vertical walls to walls laid at an angle of 30° with the centre line of the coke oven chamber. Thermal and mechanical disadvantages incidental to these methods have led to the trial of a changed method of reversing the heating gases, a unit being erected in which the combustion gases travel upwards through the whole of the 36 heating flues of one pillar disposed in groups to a long horizontal channel level with the top of the coke, pass through three or four insulated ducts over the top of the oven, and then flow downwards into vertical flues in an adjoining pillar.⁹¹ This method should eliminate unheated sections due to choking of the fireclay nozzles used (*cf.* also L. Wilputte⁹²).

A brief account of the 10-oven compound regenerative unit⁹³ erected for the Team By-Product Coke Oven Co. under E.P. 175,312 has been given; it is claimed that the chimney gases leaving the battery have an average temperature about 180° C.

Heat balances for batteries of coke ovens have been determined by D. S. Chamberlin and E. W. McGovern,⁹⁴ and by D. W. Wilson, H. O. Forrest, and C. H. Hertz.⁹⁵ Attention is drawn to the heat loss by the hot coke, and a number of patents cover the dry cooling of coke with utilisation of the heat by means of an inert gaseous carrier caused to flow in a cycle through the coke in a cooling chamber and through a steam generator^{96,97}; a thermal efficiency of 78% is claimed, from which must be deducted 8% on account of steam absorbed by the circulating fan. R. Düll⁹⁸ moves the coke through the heat exchanger on a travelling grate. The production of water-gas by coke quenching is referred to in several patents.⁹⁹

The physical properties of metallurgical coke in their bearing on the carbon function in the blast furnace have received further

⁹¹ J. Becker, E.P. 171,117.

⁹² E.P. 202,197; *J.*, 1923, 44A.

⁹³ *Iron and Coal Trades Review*, 1923, May, 18 E.P. 175,312.

⁹⁴ *Gas World*, 1923, 78, *Coking Sect.*, 42; *J.*, 1923, 436A.

⁹⁵ *Ind. Eng. Chem.*, 1923, 15, 251; *J.*, 1923, 389A.

⁹⁶ Sulzer Frères, E.P. 173,762, 187,567, 192,182; *J.*, 1923, 539A, 258A.

⁹⁷ Gelsenkirchener Bergwerke A.-G., E.P. 183,113; *J.*, 1923, 485A; *cf.* also Eigner, *Gas- u. Wasserfach*, 1922, 65, 732.

⁹⁸ E.P. 191,235; *J.*, 1923, 215A.

⁹⁹ O. Rosenthal, G.P. 369,315. P.v.d. Forst, G.P. 363,186; *J.*, 1923,

438A. Sulzer Frères, E.P. 173,763; *J.*, 1923, 300A.

attention.¹⁰⁰ E. R. Sutcliffe and E. C. Evans¹⁰¹ claim that the employment of coke prepared by their method,¹⁰² and having minute cells with thin cell walls, would concentrate the process of reduction nearer to the hearth, and that less limestone and lower volume of blast would be required, with consequent reduction in the sensible heat leaving the furnace; also that the increased amount of direct reduction would reduce the carbon requirements and increase the output of the furnace. The blast furnace experiments of G. St. J. Perrott and S. P. Kinney¹⁰³ do not seem wholly to agree with these deductions.

Methods of measuring the reactivity of coke have been discussed by a number of workers. R. V. Wheeler¹⁰⁴ heats a graded sample at a definite temperature in a current of oxygen at 400° C. or of carbon dioxide at 900° C. From the oxidation reaction constant, the order of combustibility observed was "active charcoal," wood charcoal, gasworks coke, patent fuel (*cf. supra*), foundry coke, while from the reduction reaction constant, the patent fuel took a prior position to the gasworks product. F. Fischer and his co-workers¹⁰⁵ have adopted the carbon dioxide reduction method, and have also determined the temperature at which the coke commences to reduce carbon dioxide to monoxide; in the course of their work they confirm the observation that any circumstance in manufacture which tends to lessen the surface by covering it with the coke residue obtained by heating tar decreases the combustibility. These chemists, and also K. Bunte and V. Kölmel,¹⁰⁶ conclude that it is the method rather than the temperature of production that mainly determines the character of the coke. K. Bunte¹⁰⁷ suggests that during carbonisation the stage 100°-400° C. should be passed through comparatively rapidly, and the stage 400°-650° comparatively slowly.¹⁰⁸ F. Heyd, *inter alia*, discusses¹⁰⁹ the effect of the composition of the inorganic matter present in the coal on the combustibility of the coke; easily reducible iron and other metallic silicates have a deleterious effect, while the alkali silicates (present in charcoal) are of minor importance. This

¹⁰⁰ Cf. *Ann. Repts.*, 1922, 7, 19.

¹⁰¹ *J. Iron and Steel Inst.*, 1923, 107, 27; *J.*, 1923, 552A.

¹⁰² Cf. *J.*, 1922, 196T, 492A.

¹⁰³ Amer. Inst. Min. and Met. Eng., 1923; *cf. J.*, 1923, 436A.

¹⁰⁴ *J. Iron and Steel Inst.*, 1923, 107, 75.

¹⁰⁵ F. Fischer, K. Breuer, and H. Brocho, *Brennstoff-Chem.*, 1923, 4, 23, 168; *J.*, 1923, 256A, 697A.

¹⁰⁶ *Gas- u. Wasserfach*, 1922, 65, 592; *J.*, 1923, 132A.

¹⁰⁷ *Brennstoff-Chem.*, 1923, 4, 167; *J.*, 1923, 697A.

¹⁰⁸ Cf. G. E. Foxwell, *Gas World*, 1923, 78, *Coking Sect.*, 48; *Abs.*, 1924, B, 4.

¹⁰⁹ *Brennstoff-Chem.*, 1923, 4, 273; *J.*, 1923, 813A, 1009A; *ibid.*, 1923, 4, 309; *Abs.*, 1924, B, 4.

opinion is opposed by F. Schreiber,¹¹¹ who regards the graphite formed by methane decomposition as the most important factor. This author is supported by G. Agde and F. Recke,¹¹² and by H. Broche,¹¹³ who suggests that the ash catalytically accelerates graphite formation.

The forms in which sulphur is present in coke is the subject of a number of papers by A. R. Powell.¹¹⁴ Coke prepared by the usual commercial processes is found to contain, before it is cooled, only two forms of sulphur—sulphur in solid solution, and ferrous sulphide with smaller quantities of other sulphides. When coke cools, even with limited access of air, oxidation of ferrous sulphide takes place with the formation of free sulphur and sulphates. When coke is quenched the decomposition of the sulphide is incomplete, due to the speed with which the temperature is brought below that necessary for oxidation. The free sulphur thus produced is adsorbed and its removal has proved difficult. When hydrogen is led through red-hot coke the sulphur removed is derived from the ferrous sulphide. Coke prepared in the laboratory contains, in addition, adsorbed sulphur which at higher temperatures passes into solid solution. The relationship of these results to the blast-furnace reactions is considered, and a method for the determination of the free sulphur is given.

The behaviour of sulphur during the gasification of coke has been studied by S. Pexton and J. W. Cobb,¹¹⁵ who find that the sulphur constituent assumed by Powell to be in solid solution could only be separated by complete gasification of the carbon. High concentrations of steam in the gases leaving the coke promoted independent decomposition of the sulphide sulphur in the early stages of gasification. The whole of the sulphur removed is in the form of hydrogen sulphide or carbon oxy-sulphide, and only 2–3% is obtained as free sulphur. A. Lissner¹¹⁶ finds that the addition of 5–10% of metallic iron exerts a beneficial effect on the desulphurisation of coke by hydrogen or chlorine; the same author has also conducted experiments on the complete removal of sulphur from the original coal.

GAS PURIFICATION.

Attention during the year has naturally been concentrated on the elimination of sulphur and cyanogen compounds. To remove

¹¹¹ *Brennstoff-Chem.*, 1923, **4**, 341; *Abs.*, 1924, B, 4.

¹¹² *Ibid.*, 1923, **4**, 341; *Abs.*, 1924, B, 4.

¹¹³ *Ibid.*, 1923, **4**, 343; *Abs.*, 1924, B, 4.

¹¹⁴ *J. Amer. Chem. Soc.*, 1923, **45**, 1; *Amer. Inst. Min. and Met. Eng.*, Feb., 1923; *Ind. Eng. Chem.*, 1923, **15**, 951; *J.*, 1923, 214A, 436A, 455A, 697A, 1000A.

¹¹⁵ *Inst. Gas. Eng.*, 1923; *J.*, 1923, 755A.

¹¹⁶ *Brennstoff-Chem.*, 1923, **4**, 305; *J.*, 1923, 1163A.

hydrogen sulphide and hydrocyanic acid, the gas is washed with an alkali carbonate solution, and the latter is then recovered by blowing with gases containing carbon dioxide,¹¹⁷ or by heating with steam accompanied by aeration¹¹⁸; in the patent covering the former method it is mentioned that the potassium salt is preferable to that of sodium, inasmuch as a more concentrated solution may be employed, and the size of the plant can be correspondingly reduced. Details are given by E. H. Bird¹¹⁹ of plants working such a purification process with capacities up to 12 million cub. ft. of gas a day; in the cases cited coal gas was purified, obtaining an 89–91% removal of hydrogen sulphide with a consumption of 0.062–0.019 lb. of soda ash per 1000 cub. ft. Alternatively, a solution containing nickel sulphate, ammonia, and ammonium sulphate may be used, the purifying material being recovered by aeration, if necessary under pressure¹²⁰; likewise, alkaline iron solutions may be employed containing sufficient oxalic acid to convert the iron present either completely, or for the most part, into ferrioxalate.¹²¹ An extension of the Koppers Co.'s patents provides for the recovery of sodium thiosulphate by crystallisation from the liquor resulting from the main process, after concentration.¹²²

Still other proposed methods for desulphurisation are absorption by lime at 600°–1000° C., with subsequent regeneration of the lime,¹²³ and adsorption by activated charcoal¹²⁴ and, indeed, if literature so far published were the sole criterion, activated charcoal would promise to be well-nigh the panacea of a gas manufacturer's ills.

To recover sulphur from the charcoal, F. Schreiber¹²⁵ suggests the use of tetralin as a solvent, and R. Kattwinkel¹²⁶ shows that the same reagent may be employed in the case of spent oxide; as a substitute A. Jaeger¹²⁷ recommends the hydrocarbon fraction boiling between 200° and 210° C., obtained by distilling a low-temperature tar.

Cyanogen compounds may be removed by treating the gas with alkaline-earth bicarbonate or carbonate in the presence of hydrogen

¹¹⁷ T. P. L. Petit, E.P. 195,061. Koppers Co., E.P. 190,116, 190,117, 190,119.

¹¹⁸ Koppers Co., E.P. 169,996; U.S.P. 1,440,977; *Gas World*, 1923, 78, 20. Cf. U.S.P. 1,436,196; *J.*, 1923, 46A.

¹¹⁹ *Chem. and Met. Eng.*, 1923, 29, 16; *J.*, 1923, 815A; cf. also W. S. Blauvelt, *Gas Age Record*, 1923, 52, 334.

¹²⁰ Ges. f. Kohlentechnik, E.P. 186,316; *J.*, 1923, 887A.

¹²¹ Badische Anilin u. Soda Fabrik, G.P. 368,245; *J.*, 1923, 642A.

¹²² The Koppers Co., E.P. 200,760.

¹²³ E. Will, *Chem. Zentr.*, 1923, 94, IV., 896; *Abs.*, 1924, B, 5.

¹²⁴ E. Will and L. Köster, *ibid.*, 1923, 94, IV., 895; *Abs.*, 1924, B, 5.

¹²⁵ *Brennstoff-Chem.*, 1922, 3, 355; *J.*, 1923, 42A.

¹²⁶ *Ibid.*, 1922, 3, 310.

¹²⁷ *Ibid.*, 1922, 3, 356; *J.*, 1923, 43A.

sulphide and ammonia, whereby cyanide is converted into ammonium thiocyanate¹²⁸; copper or even presence of ammonia forms the subject of a patent¹²⁹ for the same purpose (this also removes hydrogen sulphide). According to another patent,¹³⁰ leaching spent gas-purifying material with solutions of soluble sulphides removes both sulphur and cyanogen compounds. A. Deleève¹³¹ gives a summarised account of the method of cyanogen extraction by conversion into sodium ferrocyanide with sodium carbonate and ferrous sulphate, and thence into Prussian Blue.

BENZOL RECOVERY FROM GAS AND BENZOL REFINING.

- Wash-oil processes for the recovery of benzol from town's gas and coke-oven gas are at present in universal practice in this country, but increasing attention is being paid to the possibilities of the use of solid adsorbents, the falling price of the product, controlled to some extent by petrol prices, necessitating attention being devoted to methods that promise a reduction in working costs or an increase in yield of the refined product.
- Benzol recovery from town's gas is now only adopted at a few favourably equipped works, and interesting figures relating to the present and potential supplies of benzol are given by W. G. Adam¹³² in his statement of evidence laid before the Ministry of Transport Committee on Motor Fuel Taxation.

A full description of the Langley Park recovery and rectification plant has been given by S. Westhorpe,¹³³ in which the factors that control the efficiency of the processes are briefly referred to and certain recommendations are made. American gas oil is found to yield good working results if the product is sold as motor spirit, and the presence of a small percentage of paraffins is thus not deleterious. Gas oil possesses the advantages of being a good naphthalene solvent, and B. Richardson¹³⁴ has described its employment for eliminating naphthalene from town's gas, the used oil serving as an enriching agent for the water-gas installation. W. B. Leech and E. Edwards, at Beckton, have developed the use of gas oil for the dual purpose of naphthalene removal and benzol recovery with marked success. K. Bunte¹³⁵ using coal tar oils,

¹²⁸ G. Tapley and W. L. Galbraith, E.P. 202,024; cf. *Ann. Repts.*, 1921, 6, 63.

¹²⁹ P. von der Forst, G.P. 361,324; *J.*, 1923, 593A.

¹³⁰ Rhein. Ver. Chem. Fabr. A.-G., G.P. 372,327.

¹³¹ *Chim. et Ind.*, 1923, 10, 632; *Abs.*, 1924, B, 5. Cf. E.P. 181,719; *J.*, 1923, 268A.

¹³² *Gas World*, 1923, 78, 504.

¹³³ *Ibid.*, 1923, 78, Coking Sect., 35; *J.*, 1923, 436A.

¹³⁴ *Gas J.*, 1923, 164, 515; *J.*, 1923, 152T. Also J. Parker, *Gas World*, 1922, 77, 235.

¹³⁵ K. Bunte, *Gas- u. Wasserfach*, 1923, 66, 490, 507; *J.*, 1923, 964A. Cf. also K. Bunte and H. Pippig, *ibid.*, 1923, 66, 657; *Abs.*, 1924, B, 5.

avoids naphthalene difficulties by adding fresh oil to the enriched liquid, submitting it to a preliminary steam distillation before use. The light oil residue after benzol distillation is cooled and the fluid fraction returned to the wash oil to reduce "ageing." The desirable maximum of naphthalene in the wash oil is placed at 10%, the method of Glaser and Metzger¹³⁶ being recommended for its determination. Other papers dealing with the control of wash oil quality have been contributed by Offe,¹³⁷ R. Geipert,¹³⁸ T. Biddulph-Smith,¹³⁹ and R. E. Wilson.¹⁴⁰ Cantelo¹⁴¹ discusses the effect of temperature on the recovery of volatile solvents from gases. F. Raschig claims¹⁴² to have reduced the expenditure of steam to 1½ times, and of cooling water to 10 times the amount of the recovered benzol, using tower scrubbers packed with Raschig rings, effective heat exchangers, and vacuum distillation of the rich oil with indirect steam as the heating medium. This paper should be read in conjunction with a valuable communication by F. Plenz, K. Bode, and T. Werner,¹⁴³ in which the complete thermal diagrams for a benzol recovery plant are given.

The theory of gas absorption by liquids is the subject of papers by W. G. Whitman,¹⁴⁴ M. B. Donald and C. W. Tyson,¹⁴⁵ and R. T. Haslam.¹⁴⁶

H. S. and M. D. Davis¹⁴⁷ describe an apparatus for vapour pressure measurements to be employed in benzol recovery process control.

Reference was made in the 1922 Report to the use of charcoal as an adsorbent. During 1923 strong claims have been advanced for the silica gel process.¹⁴⁸ An article by Rex Furness¹⁴⁹ serves as a useful introduction to the comparison of the oil and solid adsorbent processes. Comparative figures for the wash oil and active carbon processes are also given by Steding.¹⁵⁰ The

¹³⁶ *J.*, 1921, 502A, 805A.

¹³⁷ *Gas- u. Wasseraufsch.*, 1923, **66**, 394, 414; *J.*, 1923, 821A, 815A.

¹³⁸ *Ibid.*, 1923, **66**, 101; *J.*, 1923, 303A.

¹³⁹ *Gas World*, 1923, **78**, *Coking Sect.*, 61; *J.*, 1923, 698A. Cf. P. Whitaker, *Abs.*, 1924, 13, 6.

¹⁴⁰ R. E. Wilson and co-workers, *Ind. Eng. Chem.*, 1923, **15**, 801, 947; *J.*, 1923, 1009A.

¹⁴¹ *Canadian Chem. and Met.*, 1922, 177, 196.

¹⁴² *Gas- u. Wasseraufsch.*, 1922, **65**, 655; *J.*, 1923, 390A.

¹⁴³ F. Plenz, K. Bode, and T. Werner, *Gas- u. Wasseraufsch.*, 1922, **65**, 433, 447; *J.*, 1923, 390A.

¹⁴⁴ *Chem. and Met. Eng.*, 1923, **29**, 146; *J.*, 1923, 914A. Cf. also *Gas World*, 1923, **78**, *Coking Sect.*, 16.

¹⁴⁵ *Trans. Inst. Chem. Eng.*, 1923; *J.*, 1923.

¹⁴⁶ *Ind. Eng. Chem.*, 1923, **15**, 1105; *J.*, 1923.

¹⁴⁷ *Ind. Eng. Chem.*, 1923, **15**, 1075; *J.*, 1923.

¹⁴⁸ Cf. W. A. Patrick, E.P. 136,543, 137,284, 159,508.

¹⁴⁹ *Chem. and Ind.*, 1923, 850.

¹⁵⁰ *Gas- u. Wasseraufsch.*, 1923, **66**, 457; *J.*, 1923, 877A.

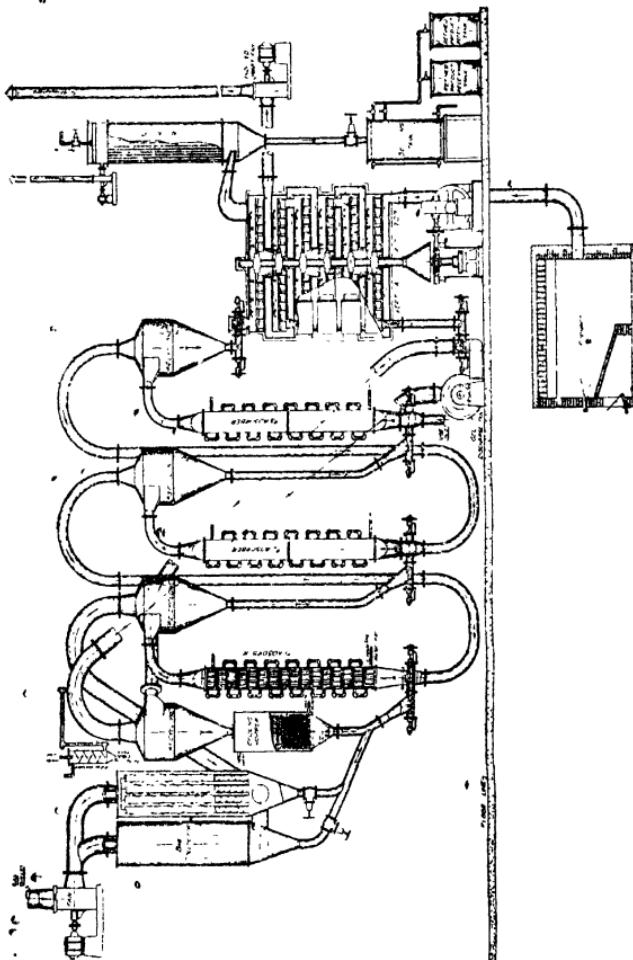
adsorptive charcoal process has been developed in Germany by the Bayer Co., and in America by the Union Carbide Laboratories, Inc.; in the first-named country it appears to have been specially applied to the recovery of volatile organic solvents, such as alcohol, ether, etc., in various branches of industry. It is claimed that a correctly prepared charcoal has a high intrinsic adsorption capacity per unit volume, and that it has also a very high selectivity for hydrocarbons and hydrocarbon derivatives, the rate of adsorption decreasing very slowly in the presence of water. Silica gel, on the other hand, is selective for water, but it possesses the following advantages:—It is prepared by relatively simple processes from cheap raw materials; it is a hard, glassy substance which can be handled with a minimum of loss; it is less readily disintegrated, and can easily be reactivated by ignition at high temperatures from time to time. The last point is of great importance in the recovery of benzol, a process in which the adsorbent is gradually poisoned by the suspended tar in the gas or by resin-forming unsaturated hydrocarbons. Adsorptive charcoal is employed in a static process, using deep filters or purifier boxes, while the recommended method for silica gel consists in blowing the powdered material, together with the gas, through a series of counter-current absorbers, and recovering the gel in dust separators of the cyclone type. The benzol is removed from the charcoal *in situ* by superheated steam at 250°¹⁵¹ and from the gel by passing it through an activator heated by furnace gases to 150° C. Periodic activation of the gel at 400°–500° C. is carried out in a horizontal rotating activator (see p. 52). There appear to be prospects of both processes being tried in this country in the near future. A full investigation of the silica gel process has been conducted by E. Williams for the National Benzole Association, but the results have not yet been published.

A paper of intense interest has been contributed by N. K. Chaney, A. B. Ray, and A. St. John.¹⁵² The authors summarise the theories relating to the action of adsorptive charcoal, its preparation, and its practical usage. Briefly, they postulate for their method of preparation the primary formation of a stable adsorption complex between the carbon and the residual hydrocarbons, and the activating process consists in the elimination of the latter by means of controlled oxidation, the stages of the process being closely followed, whereby a product of determined optimum density is produced. Carbons are obtained of a higher adsorptive capacity than silica gel, but in the practical application

¹⁵¹ Cf. E. Berl and W. Schwebel, *Z. angew. Chem.*, 1923, **36**, 541, 552; *J.*, 1923, 1210A.

¹⁵² *Ind. Eng. Chem.*, 1923, **15**, 1244.

thereof one has to remember that a circulating reagent of a low index figure is often of more value than a static mass of material possessing a greater power of adsorption.



The manufacture of adsorptive charcoals is also the subject of papers by A. B. Ray,¹⁵³ and by O. Ruff,¹⁵⁴ and his co-workers.¹⁵⁵ The recovery process has been the subject of patents by the

¹⁵³ *Chem. and Met. Eng.*, 1923, **29**, 354.

¹⁵⁴ *Kolloid-Zeits.*, 1923, **32**, 225; *J.*, 1923, 644A.

¹⁵⁵ Cf. also J. Driver and J. B. Firth, *Chem. Soc. Trans.*, 1922, **121**, 2409 *J.*, 1923, 81A, and J. B. Firth, *J.*, 1923, 242T.

Gasoline Corporation,¹⁵⁶ and by the Bayer Co.¹⁵⁷. A valuable bibliography is appended to Ray's paper.

An ingenious apparatus which admits of continuous adsorption, recovery, and reactivation of the charcoal in one unit is patented by Meister Lucius, und Brüning.¹⁵⁸ The charcoal is carried in a hollow rotor, having a series of radial compartments which consecutively pass through zones connected to rich gas, steam, and stripped gas supplies.

E. Berl and K. Andress¹⁵⁹ describe a simple method for determining absorbing power by measuring the temperature rise in a calorimeter on addition of a known weight of the absorbent to 10 c.c. of benzene. Laboratory apparatus for the determination of condensable hydrocarbons has been described by F. Haber¹⁶⁰ and by R. Kattwinkel.¹⁶¹ In both cases the condensed vapours are recovered by means of superheated steam. A. Krieger¹⁶² has examined the discrepancies of the method, and engages in polemic with R. Kattwinkel.¹⁶³ A. L. Davis¹⁶⁴ claims greater accuracy for a process involving the distillation of the rich charcoal with cresol, the latter being removed from the distillate with caustic soda.

Some properties of silica gels are considered in a communication by E. Berl and W. Urban.¹⁶⁵ A paper by E. M. Faber and his co-workers¹⁶⁶ demonstrates the long economic life of silica gels when employed in removal of pure substances such as water or benzene from air, but does not deal with practical cases in which "poisons" are present. The Bayer Co.¹⁶⁷ in the manufacture of silica gel submits the hydrosol first formed to pressures up to 350 atmospheres to remove a large fraction of the water, and then wash and dry at gradually increasing temperatures up to 200° C. Other solid inorganic adsorbents referred to in the literature are fuller's earth¹⁶⁸ and iron hydroxide gel.¹⁶⁹

Another important use which may be considered here is the employment of silica gel for the purification of petroleum and

¹⁵⁶ U.S.P. 1,453,215; *J.*, 1923, 1060A.

¹⁵⁷ G.P. 310,092; *J.*, 1921, 204A.

¹⁵⁸ E.P. 187,223; *J.*, 1923, 386A.

¹⁵⁹ *Z. angew. Chem.*, 1922, **35**, 722; *J.*, 1923, 127A.

¹⁶⁰ *Chem.-Zeit.*, 1923, **47**, 62; *J.*, 1923, 176A.

¹⁶¹ *Brennstoff-Chem.*, 1923, **4**, 179; *J.*, 1923, 699A; *Chem.-Zeit.*, 1923, **47**, 682; *Abs.*, 1924, B, 6.

¹⁶² *Chem.-Zeit.*, 1923, **47**, 357; *J.*, 1923, 538A.

¹⁶³ *Chem.-Zeit.*, 1923, **47**, 682; *Abs.*, 1924, B, 6.

¹⁶⁴ *Ind. Eng. Chem.*, 1923, **15**, 689; *J.*, 1923, 813A.

¹⁶⁵ *Z. angew. Chem.*, 1923, **36**, 57; *J.*, 1923.

¹⁶⁶ E. M. Faber, H. G. Olson, and W. A. Taylor, *Chem. and Met. Eng.*, 1923, **28**, 805; *J.*, 1923, 604A.

¹⁶⁷ E.P. Appl. 24,495 of 1923.

¹⁶⁸ K. Ikeda, E.P. 202,795; *J.*, 1923, 1011A.

¹⁶⁹ B. Lambert, E.P. 188,786; *J.*, 1923, 39A.

benzol distillates. The removal of sulphur compounds from petroleum distillates by this process is now an adopted practice on the large scale, and its application to benzol is under consideration. A. C. Fieldner and G. W. Jones¹⁷⁰ find that agitation of crude benzol, distilling up to 143° C., with 2·5% of its weight of sodium hydroxide, followed by percolation through the gel, yields a motor fuel free from the gum-forming substances present in the crude oil, together with improved recovery as compared with the customary acid process. The sulphur content, mainly due to carbon bisulphide, is reduced by subsequent careful fractionation. It is to be noted that the product would not pass the present accepted specifications as regards either colour or the acid test for unsaturated compounds.

An interesting paper bearing upon corrosion by motor fuels has been published by W. R. Ormandy and E. C. Craven,¹⁷¹ who have noted the presence of, and determined quantitatively the free sulphur present in various petrols and benzols. British motor benzols, as a general rule, were found to be free from this impurity, but not so continental samples. In the latter case, the use of highly concentrated sulphuric acid in washing may be a contributing factor; and in both cases, imperfect fractionation before acid treatment,¹⁷² and high temperatures during the washing process are the probable cause.

GAS ANALYSIS.

But few matters of outstanding interest are to be chronicled in the analysis of coal gas. A modified form of Hempel explosion pipette designed to eliminate leakage is described by K. Tiddy,¹⁷³ a new Bunte pipette by A. Krieger,¹⁷⁴ and an exact gas burette by H. J. M. Creighton.¹⁷⁵ An automatic carbon monoxide recorder is described by G. B. and H. S. Taylor¹⁷⁶; this instrument depends on the conversion of the monoxide into dioxide, absorption of the latter by standard ammonia, and determination of the variation of electrical resistance of the resulting solution; an accuracy of 0·2% is claimed. The determination of hydrogen in producer-gas has called forth an instrument designed by Siemens u. Halske A.G.,¹⁷⁷ which depends on the variation in thermal conductivity of

¹⁷⁰ *Chem. und Met. Eng.*, 1923, **29**, 543; *J.*, 1923, 1058A; cf. also E.P. 190,553; *J.*, 1923, 174A, and F. G. P. Remfry, E.P. 205,868; *Abs.*, 1924, B, 9.

¹⁷¹ *J. Ind. Petrol. Tech.*, 1923, **9**, 133; *J.*, 1923, 591A.

¹⁷² Cf. P. Dekker, *Chem. Weekblad*, 1923, **20**, 575; *J.*, 1923, 1168A. H. D. Muller and S. Langedijk, *ibid.*, 1923, **20**, 627; *Abs.*, 1924, B, 9.

¹⁷³ *Gas World*, 1923, **79**, 187.

¹⁷⁴ *Chem.-Zeit.*, 1922, **46**, 1060; *J.*, 1923, 76A.

¹⁷⁵ *Trans. Nova Scotian Inst. Sci.*, 1919-20, **15**, 115; *J.*, 1923, 1045A.

¹⁷⁶ *J. Ind. Eng. Chem.*, 1922, **14**, 1008; *J.*, 1923, 76A.

¹⁷⁷ K. Wilhelm, *Feuerungstechn.*, 1923, **11**, 171; *J.*, 1923, 591A.

the gas, this being found by the electrical resistance of two wires which varies with temperature. An apparatus for determining the moisture content of a water-gas is described by R. Lant.¹⁷⁸ The principle involved depends on the local reduction in pressure caused by a baffle or constriction in the pipe through which the gas is passing. If two constrictions be used, and the water vapour be removed between them, the additional loss in pressure is a measure of the volume of the aqueous vapour. It is claimed that the average error is about 1%. A portable gas apparatus of the Orsat type is the subject of a patent by D. M. Macdonald¹⁷⁹ and the determination of carbon dioxide in gases of a paper by H. Strade and K. Kling¹⁸⁰ A device for finding the specific gravity of natural gas is described by T. R. Weymouth, R. P. Anderson, and J. R. Fay,¹⁸¹ and a discussion of the methods used in determining accurately the densities of industrial gases is contributed by M. S. Blanchard.¹⁸² A new automatic pressure and temperature corrector for gas volumes—an improvement for the Beasley recorder—is described by C. H. Beasley.¹⁸³

R. Kattwinkel¹⁸⁴ in view of the fact that small amounts of carbon dioxide are not determined accurately by cuprous chloride, recommends the use of iodine pentoxide in such cases, the reaction proceeding rapidly and quantitatively at 110°–120° C. It is necessary first to remove unsaturated hydrocarbons; this he accomplishes by the use of charcoal. A reagent frequently employed in practice to achieve this end is a solution of bromine, but F. S. Sinnatt and L. Slater¹⁸⁵ have found that by this method some volatile compound is produced which is not absorbed, and consequently as much as 0·012% of carbon monoxide may be indicated in a gas which is really free from it: hence they suggest substituting 10% fuming sulphuric acid for the bromine solution; normal results are thus obtained.

Sulphur dioxide in flue gases is determined by K. Balthasar¹⁸⁶ by passing the gas through 25% caustic soda, acidifying with acetic acid, and titrating with iodine. Naphthalene is determined in coal gas¹⁸⁷ by passing the gas through a standard solution of picric acid and determining the increase in the electrical resistance

¹⁷⁸ *Gas- u. Wasserfach*, 1922, **65**, 257, 277; *J.*, 1923, 590A.

¹⁷⁹ E.P. 201,408.

¹⁸⁰ *Feuerungstech.*, 1922, **11**, 13.

¹⁸¹ *Ind. Eng. Chem.*, 1923, **15**, 358; *J.*, 1923, 436A.

¹⁸² *Chem. and Met. Eng.*, 1923, **29**, 399.

¹⁸³ *J.*, 1923, 457T.

¹⁸⁴ *Brennstoff-Chem.*, 1923, **4**, 104; *J.*, 1923, 389A.

¹⁸⁵ *Fuel*, 1922, **1**, 241; *J.*, 1923, 133A.

¹⁸⁶ *Chem.-Zeit.*, 1923, **4**, 225; *J.*, 1923, 391A.

¹⁸⁷ H. Fulweiler, U.S.P. 1,443,330; *J.*, 1923, 259A.

of the resulting solution; ethylene is determined¹⁸⁸ by treating the gas with 87% sulphuric acid (which absorbs only higher olefines) and subsequently applying the bromine water method. In connexion with ethylene absorption, W. Traube and R. Justh¹⁸⁹ point out that a mixture of chlorosulphonic acid and sulphuric acid is as efficacious as is fuming sulphuric acid for analytical purposes, whilst commercially it has the advantage of more readily yielding derivatives of ethylene of technical value.

J. W. Whitaker¹⁹⁰ directs attention to the fact that in determining methane in mine airs by slowly burning it in contact with a heated platinum spiral, the latter must be raised to a white heat, and the gas exposed to the action of it for 3/4 minutes; otherwise the methane is not completely oxidised.

Qualitative tests for discovering the presence of small amounts of hydrocyanic acid by picrate, guaiacum, and phenolphthalein are given by S. H. Katz and E. S. Longfellow.¹⁹¹

Some notes by J. W. Wood on gas calorimeters and other instruments used in gas works will be found at the end of this report.

CORROSION.

The corrosion of iron materials employed in gas engineering has again occasioned a number of contributions. H. E. Williams¹⁹² maintains that the internal corrosion of pipes is caused chiefly by the coincident action of carbon dioxide, moisture, and air; he considers that this is accelerated by the removal of the condensate of tarry matter and heavy hydrocarbons in the pipes consequent on the decrease in the illuminative power of the gas; and that any hydrocyanic acid is innocuous, and not germane to the corrosion, though it is secondarily absorbed by the iron oxides. On the other hand, H. G. Colman¹⁹³ maintains that the part played by traces of ammonia and hydrocyanic acid producing a porous layer of ferrocyanides is of importance: he is of opinion that these gases in conjunction accelerate the rate, and particularly the initial stage of corrosion—the bulk of which is effected by the carbon dioxide and oxygen in the gas. B. Richardson¹⁹⁴ considers this phase of the hydrocyanic acid problem is but secondary. In

¹⁸⁸ H. Tropsch and A. von Philippovich, *Brennstoff-Chem.*, 1923, **4**, 147; *J.*, 1923, 591A.

¹⁸⁹ *Brennstoff-Chem.*, 1923, **4**, 150; *J.*, 1923, 591A.

¹⁹⁰ *Fuel*, 1923, **2**, 202; *J.*, 1923, 698A.

¹⁹¹ *J. Ind. Hyg.*, 1923, **5**, 97; *J.*, 1923, 853A.

¹⁹² *Gas J.*, 1923, **162**, 725; *J.*, 1923, 699A; cf. also B. Richardson, *Gas J.*, 1923, **164**, 515.

¹⁹³ *Gas J.*, 1923, **163**, 794; *J.*, 1923, 756A. See also Tapley, *Gas World*, 1923, **78**, 460.

¹⁹⁴ *Gas World*, 1923, **78**, 462, 468.

this connexion it may be pointed out that U. R. Evans¹⁹⁵ shows that if free access of air to the metal be prevented, corrosion is limited to a small area, which is then rapidly attacked, thus explaining the rapid corrosion in "pits" and areas covered by porous corrosion products, and J. H. G. Monypenny¹⁹⁶ demonstrates that ammonium chloride solutions exert a staining and pitting action even on "stainless" steel.

Bertelsmann¹⁹⁷ enumerates the desiderata for the media in which pipes should be laid — porous soil, a channelling of sand, freedom from acid water, and absence of stray electric currents; he further recommends a neutral oil as an efficient protection for the metal parts of a gas meter, and suggests that the only real remedy for internal corrosion of gas pipes is adequate purification of the gas—a suggestion emphatically endorsed by B. Richardson (*loc. cit.*).

B. Zschokke,¹⁹⁸ in view of the known protective action of chromates, recommends that iron structures be coated with an emulsion of grease and a solution of an alkali chromate; also that the metal in reinforced concrete be covered with a layer of concrete containing a soluble chromate, whilst R. J. Milbourne¹⁹⁹ strongly urges the construction of gasholders of wrought iron in place of mild steel on account of the less corrosion experienced by the former.

Articles dealing with the gas-works application of the more popular anti-corrosive paints have been contributed by J. G. Bearn²⁰⁰ and H. Chaloner,²⁰¹ and attention may be directed to a new volume on "The causes and prevention of corrosion," by A. Pollitt (Benn Bros.).

AMMONIA AND AMMONIUM SULPHATE.

The possibilities of increasing the yield of ammonia in the carbonisation of coal have received further attention. R. A. Mott and H. J. Hodson²⁰² have given their experimental results to show the effect of contact materials, and of the nature of the atmosphere on the dissociation of ammonia. Water vapour exercised an inhibiting effect; a small proportion of oxygen produced a similar result, possibly due to preferential union with hydrogen to produce water vapour. In hydrogen the decomposition

¹⁹⁵ Inst. Metals, Sept., 1923; *Trans. Faraday Soc.*, 1923, **19**, 201; *J.*, 1923, 458A, 983A.

¹⁹⁶ Faraday Soc., April, 1923; *J.*, 1923, 457A.

¹⁹⁷ *Gas- u. Wasserfach*, 1922, **65**, 686; *J.*, 1923, 133A.

¹⁹⁸ *Rev. Met.*, 1923, **20**, 165.

¹⁹⁹ *Gas World*, 1923, **79**, 445.

²⁰⁰ *Ibid.*, 1923, **78**, 206.

²⁰¹ *J.*, 1923, **78**, 139.

²⁰² *J.*, 1923, **4**, 26, 29T.

was less than in coal gas, but was increased by nitrogen. R. A. Mott²⁰² from a consideration of earlier work of the Leeds group²⁰³ suggests previous removal of ferruginous ash and rebuilding of old oven walls, thereby minimising catalytic decomposition, coupled with steaming during the 22nd to 26th hours of the coking period, a period during which ammonia evolution is greatest and thermal decomposition high. G. E. Foxwell²⁰⁴ criticises the financial aspect of the proposition.

High yields of ammonium sulphate have been obtained from the vertical retorts at the Coatbridge Gas Works under the relatively low carbonising temperatures possible with Scottish coals, and the beneficial effect of the fairly heavy steaming employed is demonstrated by G. Braidwood.²⁰⁵ The passage of blue water-gas into the base of the retort was shown to be of no assistance under the conditions cited. H. F. Krau²⁰⁶ reports increased yields of ammonia by steaming in horizontal retorts with simultaneous production of water-gas, likewise by cooling the free space in the retort by introducing water-gas during distillation, while N. Christmann²⁰⁷ quotes the results of further experiments on the influence of alkaline-earth carbonates on the gasification of fixed nitrogen in coke with steam and air. In continuation of the work of A. C. Monkhouse and J. W. Cobb,²⁰⁸ S. Pexton and J. W. Cobb²⁰⁹ have further studied the action of steam in liberating nitrogen and sulphur from cokes prepared in different ways and conclude, *inter alia*, that the proportion of nitrogen recovered as ammonia is dependent on the concentration of undecomposed steam in the exit gases and on the temperature of gasification. It is shown that considerable nitrogen is recoverable as ammonia from soft and medium cokes without gasification of the corresponding percentage of free carbon, but not from very hard cokes. Present-day gas-works practice for ammonia recovery is reviewed by F. Plenz²¹⁰ and recommendations are made for efficient plant control.

The production of neutral ammonium sulphate in this country has reached 70% of the total manufacture²¹¹; a number of patents covering new processes or plant have been published, but they involve no new principles. The contributions on this subject in

²⁰² *Gas World*, 1923, **78**, Coking Sect., 21.

²⁰³ *Ann. Repts.*, 1922; *J.*, 1923, 4T.

²⁰⁴ *Gas World*, 1923, **78**, Coking Sect., 22, 47.

²⁰⁵ G. Braidwood, *Gas World*, 1923, **78**, 637; *J.*, 1923, 755A.

²⁰⁶ *Gas- u. Wasserfach*, 1922, **65**, 532; *J.*, 1923, 132A; cf. *Gas J.*, 1921,

153, 804, and other earlier work.

²⁰⁷ *Gas- u. Wasserfach*, 1923, **66**, 249; *J.*, 1923, 590A.

²⁰⁸ *Gas J.*, 1922, **158**, 828; *J.*, 1922, 532A.

²⁰⁹ *Ibid.*, 1923, **163**, 160; *J.*, 1923, 755A.

²¹⁰ *Gas- u. Wasserfach*, 1923, **66**, 97; *J.*, 1923, 299A.

²¹¹ *British Sulphate of Ammonia Federation Report*, 1923; *Chem. and Ind.*, 1923 [cf. *Chim. et Ind.*, 1923, **9**, 183, for the French figures].

the columns of the *Gas World* and *Chemical Age* for February, March, and April are of interest to the small manufacturer.

The Chief Inspector of Alkali Works²¹² draws attention to the lack of scientific control prevailing in many ammonium sulphate works, thus leading to reduced economy of working and accentuating the difficulty of disposing of spent liquor. Interesting data relative to lime use and volume of effluent liquors are quoted. A paper by P. Parrish²¹³ provides a sound basis for the investigation of plant conditions, and subsequent attainment of good results.

- A method of removing phenols and similar substances from spent liquor by means of furnace gases²¹² is stated to have yielded improved results, analyses indicating a volatilisation of 71% of the phenols with a reduction of 42% in the oxygen absorption figure. The method gives no definite reduction of the thiocyanate and thiosulphate present, but the employment of two gassing towers in series to effect substantial removal of the phenols, followed by the action of bacteria on specially prepared filter beds, promises greater success in the reduction of the oxygen absorption figure.²¹⁴

A number of methods for the recovery or utilisation of ammonia from coal gas without prior manufacture of sulphuric acid have been examined. In a process developed in connexion with a synthetic ammonia plant, a mixture of ammonia, sulphur dioxide, and oxygen is passed through a tower against a descending spray of water or ammonium sulphate solution.²¹⁵ C. Still²¹⁶ washes coal gas with strong sodium chloride solution, and treats the liquor leaving the washer with carbon dioxide in excess to produce sodium bicarbonate and ammonium chloride. E. L. Pease²¹⁷ produces a compound fertiliser by employing as the ammonia-extracting material in a trough fitted with a rotating worm a prepared base obtained by heating peat with a dilute solution of crude phosphoric acid and potassium sulphate (the ammonia in the gas being recovered as a phosphate). The proof of the economy of this process will be awaited with interest. A general survey of the direct use of ammoniacal liquor for fertilising purposes has been published.²¹⁸

²¹² Cf. J., 1922, 317R; Gas J., 1922, 159, 213.

²¹³ J., 1922, 229T; Proc. Chem. Eng. Group, 4.

²¹⁴ Ann. Repts., 1922, 7, 172 et seq. Also G.P. 362,378, 370,151.

²¹⁵ Elektrizitätswerk Lonza A.-G. and H. Danneel, G.P. 369,888; J., 1923, 490A.

²¹⁶ G.P. 371,702. Cf. U.S.P. 1,384,141; J., 1921, 623A.

²¹⁷ Gas World, 1923, 79, Coking Sectt., 80. See also E.P. 191,415.

²¹⁸ Gas- u. Wasserfach, 1923, 66, 25.

was less than in coal gas, but was increased by nitrogen. R. A. Mott²⁰² from a consideration of earlier work of the Leeds group²⁰³ suggests previous removal of ferruginous ash and rebuilding of old oven walls, thereby minimising catalytic decomposition, coupled with steaming during the 22nd to 26th hours of the coking period, a period during which ammonia evolution is greatest and thermal decomposition high. G. E. Foxwell²⁰⁴ criticises the financial aspect of the proposition.

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²⁰² *Gas World*, 1923, **78**, Coking Sect., 21.

²⁰³ *Ann. Repts.*, 1922; *J.*, 1923, 4T.

²⁰⁴ *Gas World*, 1923, **78**, Coking Sect., 22, 47.

²⁰⁵ G. Braidwood, *Gas World*, 1923, **78**, 637; *J.*, 1923, 755A.

²⁰⁶ *Gas- u. Wasserfach*, 1922, **65**, 532; *J.*, 1923, 132A; cf. *Gas J.*, 1921,

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²⁰⁷ *Gas- u. Wasserfach*, 1923, **66**, 249; *J.*, 1923, 590A.

²⁰⁸ *Gas J.*, 1922, **158**, 828; *J.*, 1922, 532A.

²⁰⁹ *Ibid.*, 1923, **163**, 160; *J.*, 1923, 755A.

²¹⁰ *Gas- u. Wasserfach*, 1923, **66**, 97; *J.*, 1923, 299A.

²¹¹ *British Sulphate of Ammonia Federation Report*, 1923; *Chem. and Ind.*, 1923 [cf. *Chim. et Ind.*, 1923, **9**, 183, for the French figures].

and A. Weindel²³⁰ suggests the following concomitant reactions for the processes that occur during low-temperature tar distillation:—Splitting-off of side chains, dehydrogenation of unstable sulphur compounds, decomposition of carboxyl groups, depolymerisation, and hydrolysis. The distillation of tars in a current of hydrogen and in presence of a contact substance is described by F. Frank,²³¹ and hydrogenation under pressure in presence of tin by M. Melamid.²³² Cracking of a low-temperature tar for conversion into permanent gas is the subject of a patent by A. Aicher.²³³

The hydrocarbons present in these tars are described by F. Schütz, W. Buschmann, and H. Wissebach,²³⁴ F. Schütz,²³⁵ F. Fischer²³⁶ (who finds optically active hydrocarbons present), F. Seidenschnur,²³⁷ J. Mareusson and M. Picard,²³⁸ and R. Weissgerber and E. Moehrle.²³⁹

Arnold²⁴⁰ maintains that iodine value is unsatisfactory as a criterion of these tars, and recommends, as the only possibility, the determination of aromatic and unsaturated hydrocarbons with dimethyl sulphate, and the unsaturated hydrocarbons alone by the mercury acetate method of Engler and Tauss.²⁴¹ On the other hand, J. J. Morgan and R. P. Soule²⁴² state that the iodine value is satisfactory, and also find that a good separation of the hydrocarbon distillate is obtained by boiling under reduced pressure with three-fifths of its own volume of liquid sulphur dioxide. By this means aromatic and cyclic unsaturated hydrocarbons are dissolved. H. Schrader and C. Zerbe²⁴³ describe a method of separating hydrocarbons by treating with successive amounts (10% by weight) of picric acid and collecting the successive crops of crystals formed after cooling.

The nature of the phenols present in these tars is dealt with by F. Schütz and his collaborators²⁴⁴—the higher the temperature of carbonisation, the more is the production of phenol favoured at

²³⁰ *Brennstoff-Chem.*, 1923, **4**, 321; *J.*, 1923, 1168A.

²³¹ *Petroleum*, 1923, **19**, 908; *J.*, 1923, 1014A.

²³² E.P. 171,367; *J.*, 1923, 218A.

²³³ G.P. 362,465; *J.*, 1923, 259A.

²³⁴ *Ber.*, 1923, **56**, 869; *J.*, 1923, 488A.

²³⁵ *Brennstoff-Chem.*, 1923, **4**, 84; *J.*, 1923, 343A.

²³⁶ *Ber.*, 1923, **56**, 1791; *J.*, 1923, 820A.

²³⁷ G.P. 369,883; *J.*, 1923, 762A.

²³⁸ *Z. angew. Chem.*, 1923, **36**, 253; *J.*, 1923, 596A.

²³⁹ *Brennstoff-Chem.*, 1923, **4**, 81; *J.*, 1923, 343A.

²⁴⁰ *Z. angew. Chem.*, 1923, **36**, 266, 545; *J.*, 1923, 596A, 1215A.

²⁴¹ *J.*, 1918, 554A; 1919, 4A.

²⁴² *Ind. Eng. Chem.*, 1923, **15**, 587, 693; *J.*, 1923, 706A, 820A.

²⁴³ *Brennstoff-Chem.*, 1922, **3**, 372; *J.*, 1923, 87A.

²⁴⁴ *Brennstoff-Chem.*, 1923, **4**, 85; *Ber.*, 1923, **56**, 1967; *J.*, 1923, 344A, 119A.

the expense of its homologues. R. Avenarius²⁴⁵ describes the carboxylic acids present, and identifies the phenols by their conversion into the corresponding carbanic and alaphanic esters; and F. Hoffmann and M. Heyn²⁴⁶ have isolated the solid phenols (a rotary retort seems to give but small amounts of these; probably local superheating is the cause).

Alkaline extraction of the crude tar for determination of phenols is discussed by P. K. Breuer and H. Broche,²⁴⁷ who claim an accuracy of 1% (on the original tar) for the procedure they adopt. The same subject is elucidated by F. Greenbaum,²⁴⁸ who shows that the optimum concentration of alkali for a distillate extraction is a 15% solution, and also quotes figures showing that 50% of the theoretical quantity of a 15% soda solution will recover 66% of the phenols removed by the full amount of alkali; whilst, 75% of the requisite alkali will remove over 90% of the phenols.

Extraction with superheated steam has also been experimented with: that at 225° dissolves the lower-boiling phenols almost completely²⁴⁹; at higher temperatures the heavier phenols are also appreciably soluble.²⁵⁰ It has been suggested²⁵¹ to use the water from these extractions as a photographic developer. An interesting observation is quoted by F. Fischer and C. Zerbe,²⁵² that cresols and phenols are satisfactorily reduced to the corresponding hydrocarbons, without deposition of carbon, by the action of hydrogen in presence of small amounts of iron sulphide, or by a feeble current of hydrogen sulphide in presence of heated semi-coke, previously heated to redness in presence of hydrogen sulphide.

Two observers²⁵³ have obtained ketones in distinct quantities in these tars, though Fischer²⁵⁴ notes that such results have not been confirmed in manufacturing practice by other workers.

The basic constituents of these tars are described by a number of investigators: a "Louise" tar contained pyridine, but a "Grefart" tar contained none²⁵⁴ (both these coals are from the Cologne neighbourhood); the significance of this difference is uncertain. Various pyridines and quinolines have also been

²⁴⁵ *Z. angew. Chem.*, 1923, **36**, 165; *J.*, 1923, 394A.

²⁴⁶ *Brennstoff-Chem.*, 1923, **4**, 209, 273; *J.*, 1923, 820A, 1009A.

²⁴⁷ *Ibid.*, 1923, **4**, 122; *J.*, 1923, 489A.

²⁴⁸ *Oesterr. Chem.-Zeit.*, 1923, **26**, 147; *J.*, 1923, 1168A.

²⁴⁹ F. Fischer and A. Jaeger, *Brennstoff-Chem.*, 1923, **4**, 241; *J.*, 1923, 920A.

²⁵⁰ F. Fischer, *Brennstoff-Chem.*, 1923, **4**, 225; *J.*, 1923, 880A.

²⁵¹ F. Fischer, H. Schrader, and A. Jaeger, *Brennstoff-Chem.*, 1923, **4**, 242; *J.*, 1923, 920A; cf. G.P. 374,005.

²⁵² *Brennstoff-Chem.*, 1923, **4**, 309; *J.*, 1923, 1168A; cf. *J.*, 1922, 891A.

²⁵³ R. Weissgerber, *Brennstoff-Chem.*, 1923, **4**, 51; Schütz, *ibid.*, 1923, **4**, 84; *J.*, 1923, 261A, 343A.

²⁵⁴ E. Fromm and H. Eckard, *Ber.*, 1923, **56**, 948; *J.*, 1923, 488A.

isolated.^{244, 255} J. J. Morgan and R. P. Soule²⁵⁶ record the fact that secondary bases invariably appear to be present in these low-temperature tars. The authors also give a critical review of the methods available for the analysis of the various groups of compounds present.

Lastly, A. Jaeger²⁵⁷ shows that the darkening of the phenol-free distillate from a low-temperature tar would seem to be due to the oxidation of certain basic compounds present—an action which light accelerates. It will be interesting later to know whether the bases responsible for this phenomenon have a pyridine structure or belong to a *p*-thiazine type of compound.

TAR : TAR PRODUCTS.

Successful results on large-scale operations are reported for types of plant patented during the past few years. Two dehydration units to the design of S. Wikner,²⁵⁸ in which the water contained in the tar is vaporised by means of coils heated by dry steam and by the vapours driven off by the steam coil, have been operated in conjunction with Hird distillation plants, increasing the distillation capacity 60%, with smoother working when the tar has a high water content. J. L. Major²⁵⁹ has effected further improvements in the design of his still, in which the feed liquid is heated under pressure in pipes passing through the body of hot liquid in the still before being discharged against a horizontal heated plate in the vapour space. A similar method is adopted by E. Schnell for treating watery lignite producer tars.²⁶⁰ A number of units on the molten metal bath principle have been erected, and the results obtained at Glastonbury²⁶¹ producing refined tar and light oils are stated to be highly satisfactory. For dehydration, the method is attractive, regularity and flexibility of operation being obtained with the minimum of supervision, coking troubles are avoided, and the plant lends itself to economic working on a relatively small scale. Complete distillation units operating under the same principle are being erected in this country and in America, and an account of the results is awaited with interest.^{262, 263} Messrs. Burt, Boulton, and Haywood have converted their pot

²⁴⁴ W. Gollmer, *Brennstoff-Chem.*, 1923, 4, 1, 19; *J.*, 1923, 137A.

²⁵⁵ *Ind. Eng. Chem.*, 1923, 15, 587; *J.*, 1923, 706A.

²⁵⁶ *Brennstoff-Chem.*, 1923, 4, 257; *J.*, 1923, 967A.

²⁵⁸ E.P. 196,399; *J.*, 1923, 597A; cf. also C. Still, E.P. 200,651; *J.*, 1923, 880A.

²⁵⁹ E.P. 114,353, 203,743; *J.*, 1918, 261A; 1923, 1114A.

²⁶⁰ G.P. 354,214; *J.*, 1923, 138A.

²⁶¹ *Gas J.*, 1923, 164, 255.

²⁶² E.P. 184,624; *J.*, 1923, 803A.

²⁶³ See E.P. 207,366.

stills to a continuous system, the inter-still connexion which prevents siphoning being described in the covering patent.²⁶⁴

An interesting description of the Raschig process has been provided by H. A. Prager.²⁶⁵ The system is continuous in operation, the tar, preheated by the hot pitch, being further heated in the first two stills by indirect steam, and in the third still by superheated water. The second and third stills are maintained under vacuum.

The Wilton Co. has continued the investigation of the possibilities of the combined distillation and cracking of tar, particularly that from vertical retorts.²⁶⁶ Apparently with a view of minimising the difficulties due to coking in the second coil heated to the higher temperature, they impart a spiral motion to the fluid by means of a continuous internal spiral fin, thus increasing the scouring action and improving the heat interchange.²⁶⁷ To facilitate replacement of the pipes in the cracking section the coils are placed side by side instead of concentrically.²⁶⁸

The dehydration of lignite producer tars is discussed in two papers,²⁶⁹ and the precautions necessary to prevent the formation of persistent emulsions of water and tar on water-gas plants are enunciated by W. W. Odell,²⁷⁰ together with methods of breaking the emulsion when formed. A centrifugal machine by Messrs. Broadbents has yielded satisfactory results with horizontal and vertical tars, reducing the water content to $2\frac{1}{2}\%$ with a 500-gallon per hour feed and a consumption of 6 h.p., but the machine has yet to be proved in operation with water-gas tars.

Aluminium oleate²⁷¹ has been used successfully where corrosion of a still was caused by a tarry emulsion of an acid character.

Tar Products.

Less than 5% of the main roads of this country present the conditions necessary for rendering fish poisoning due to drainage from tarred roads a pertinent question, and hence the Ministry of Transport, in framing new specifications for road tar, has not found

²⁶⁴ F. J. China, and Burt, Boulton, and Haywood, E.P. 188,575; *J.*, 1923, 48A.

²⁶⁵ *Gas World*, 1923, **79**, 118; *J.*, 1923, 920A.

²⁶⁶ Cf. W. A. Walmsley, *J.*, 1922, 296T. E.P. 127,700; *J.*, 1919, 529A.

²⁶⁷ E.P. 201,206; *J.*, 1923, 915A.

²⁶⁸ T. O. Wilton, and Wilton Chem. Eng. Co., Ltd., E.P. 200,933; *J.*, 1923, 920A.

²⁶⁹ E. Schnell, *Z. angew. Chem.*, 1923, **36**, 254; *J.*, 1923, 596A; H. Tropsch, *ibid.*, **36**, 277; *J.*, 1923, 645A.

²⁷⁰ U.S. Bureau of Mines Tech. Paper 304; *J.*, 1922, 363A; cf. also H. A. Gill, E.P. 195,876.

²⁷¹ 59th Annual Rept. H.M. Alkali Inspectors; *Chem. and Ind.*, 1923, 1023.

it necessary unduly to lower the maximum permissible phenol content nor to institute tests for bases. The importance of consistency is recognised, and the desirable limits of this physical property for the surface treating and macadam qualities is defined in terms of the Hutchinson instrument, and the limiting content of method of determination of naphthalene are placed on a quantitative basis.²⁷¹ A useful paper by D. C. Broome discusses the quantitative effect on consistency of temperature and of varying additions of bitumen and mineral filler.²⁷² The surface dressing of macadam and concrete surfaces with emulsions of anthracene oil, tar, or bitumen and water is stated to have given good results, and one method of preparing the emulsion is given by J. A. Vielle.²⁷³

The determination of the viscosity of tar by means of the Stormer instrument is described by W. G. Huff, and an equation for viscosity-temperature curves is given.²⁷⁴ It was not found possible to correlate the viscosity of tars with their chemical characteristics; this was only to be anticipated in view of the number of constituents of different chemical classifications found in tars prepared under the numerous modern variations of carbonising methods. Literature frequently quotes the isolation of a compound from tar without defining the origin and nature of the raw material, and one therefore welcomes the publication of the paper by J. M. Weiss and C. R. Downs,²⁷⁵ in which the isolation, and, in many instances, quantitative determination of a considerable number of constituents of a coke-oven tar are given. R. L. Brown and R. D. Howard²⁷⁶ have identified and determined the percentage of indene and styrene in two samples of water-gas tar.

An ingenious cooler tray for pitch is described by C. Still.²⁷⁷ The desirable properties of pitches for a number of industrial purposes have also been given.²⁷⁸

Careful work on the vapour pressures and latent heats of naphthalene, anthracene, phenanthrene, and carbazole has been published by C. F. Senseman and O. A. Nelson,²⁷⁹ who show incidentally that the boiling point of carbazole is 354.76° C. and not 351.5°, as quoted in the literature. The preparation of a sample of pure naphthalene exhibiting the property of double refractivity is the subject of a note by W. Kirby²⁸⁰; the specific gravity at

^{271A} Ministry of Transport "General Directions and Specifications Relating to Tar Treatment of Roads."

²⁷² J., 1923, 192T.

²⁷³ E.P. 196,950; J., 1923, 643A.

²⁷⁴ Ind. Eng. Chem., 1923, 15, 1026; J., 1923, 1167A.

²⁷⁵ Ibid., 1923, 15, 1022; J., 1923, 1167A.

²⁷⁶ Ibid., 1923, 15, 1147; Abs., 1924, B, 48.

²⁷⁷ E.P. 200,460; J., 1923, 821A.

²⁷⁸ B. Lampe, J., 1923, 569A, 1193A.

²⁷⁹ Ind. Eng. Chem., 1923, 15, 382, 621; J., 1923, 543A, 706A.

²⁸⁰ J., 1923, 58T.

$15^{\circ}/15^{\circ}$ was 1.185, and the crystallising and melting points 80.2° and 80.7° C. , respectively. The known method of removing carbazole from crude anthracene by means of its alkali salt is varied by H. D. Gibbs,²⁸¹ who heats the press cake with alkali to convert the carbazole into an alkali salt, and then further heats to sublime the anthracene fractionally. Data relating to the solubility of phenanthrene in various organic solvents have been contributed by H. Henstock.²⁸²

Although the property of vertical-retort tar oils and phenols of giving pink or purple coloured emulsions or solutions has been investigated in a number of works' laboratories, very little information has been communicated to the scientific journals. G. S. Currey,²⁸³ led to investigate the matter by colour formation in the spent liquor from an ammonium sulphate plant, has examined the phenols of a vertical-retort tar and has isolated or obtained definite indication of the presence of the polyhydric phenols, catechol, resorcinol, and pyrogallol, mainly the first-named, in addition to the monohydric phenols derived from aromatic and hydroaromatic hydrocarbons. A methyl ether (possibly guaiacol) was isolated from the mixed phenols from the ammoniacal liquor. Disinfectants producing white emulsions are obtained by fractionation of the distillates, rejecting all oils boiling above 230° C.

Details have been given by H. T. Clarke and E. R. Taylor²⁸⁴ for the preparation of the three xylenes in a pure condition from commercial xylene, chemical methods being necessary in addition to close fractional distillation. The conditions of operation of rectifying columns have received theoretical treatment in a number of papers published in the American Journals.²⁸⁵ F. H. Rhodes²⁸⁶ recommends the single condenser as preferable to the partial condenser method, it giving greater ease of control, and constancy of the reflux distillate ratio under varying conditions. The single condenser method works well when applied to the distillation of high-boiling liquids.

The toxicity of benzene and its homologues has been the subject of recent papers, and attention is drawn to the ease of preventing poisoning by efficient ventilation, a limit of 1 part of benzene vapour in 100,000 of air being regarded as an advisable maximum.²⁸⁷

²⁸¹ U.S.P. 1,456,848; *J.*, 1923, 707A.

²⁸² *Chem. Soc., Trans.*, 1922, **121**, 2124; *J.*, 1922, 975A.

²⁸³ *J.*, 1923, 379T.

²⁸⁴ *J. Amer. Chem. Soc.*, 1923, **45**, 830; *J.*, 1923, 394A.

²⁸⁵ B. F. Dodge, *J. Ind. Eng. Chem.*, 1922, **14**, 1062; W. H. Rodebush, *ibid.*, 1922, **14**, 1036; W. A. Peters, jun., *ibid.*, 1923, **15**, 402; C. C. van Nuyts, *Chem. and Met. Eng.*, 1923, **28**, 207, 255.

²⁸⁶ *Chem. and Met. Eng.*, 1923, **28**, 590; *J.*, 1923, 479A.

²⁸⁷ E. B. Starr, *J. Ind. Hyg.*, 1922, **4**, 203; F. P. Underhill and B. R. Harris, *ibid.*, 1923, **4**, 491; *J.*, 1923, 596A.

The addition of boric acid to the sulphuric acid used for washing crude benzol is stated to result in a reduction of about 25% in the resinous matter formed, and an average increase of 2% in the yield of benzol²⁸⁸; the same reagent has been employed to remove unsaturated hydrocarbons, operating in an autoclave at 250° C.²⁸⁹ R. Kattwinkel has examined²⁹⁰ a sample of acid resin from a benzol plant, and quotes the results of its ultimate analysis. He concludes that the aromatic sulphur compounds are in the form of sulphon-acid esters, which are neutral and saturated.

ANALYSIS.

Arylsulphonido-amides of alkali metals,²⁹¹ $\text{Ar-SO}_2\text{NIM}$, are recommended as a convenient source of hypoiodous acid in the determination of phenol or salicylic acid, chloramine T being a corresponding suitable chloro-reagent. Analytical methods for determining phenol, more particularly in the control of the manufacture of phenol-formaldehyde condensation products, are discussed by W. R. Ormandy and E. C. Craven.²⁹² J. B. Hill²⁹³ examines the sources of discrepancy in the determination of phenols in coal tar oils by extraction with sodium hydroxide solution. A contribution by R. Sieber²⁹⁴ is worthy of study by those responsible for the control of the causticising process on carbolic acid plants.

J. M. Taylor²⁹⁵ discusses critically the determination of sulphur and some of its compounds, his recommendations being based on a wide experience gained at the United Alkali Co.'s central laboratory. An improvement in Metzger's method²⁹⁶ for the determination of naphthalene in tar oils has been developed.²⁹⁷

Determination of refractive index is suggested as a convenient method for the examination of liquid fuels by H. Eckart,²⁹⁸ who gives the physical constants concerned—a test obviously not intended to be applied to complicated mixtures.

The results of the labours of the Standardisation Committees of the Institute of Petroleum Technologists have been published,²⁹⁹

²⁸⁸ R. Kattwinkel, *Brennstoff-Chem.*, 1922, **3**, 357; *J.*, 1923, 48A.

²⁸⁹ A. Jaeger, *ibid.*, 1923, **4**, 260; *J.*, 1923, 967A.

²⁹⁰ R. Kattwinkel, *ibid.*, 1923, **4**, 55; *J.*, 1923, 261A.

²⁹¹ E. Roberts, *Chem. Soc. Trans.*, 1923, **123**, 2707; *J.*, 1923, 1215A.

²⁹² *J.*, 1923, 18T.

²⁹³ *Ind. Eng. Chem.*, 1923, **15**, 799; *J.*, 1923, 1014A.

²⁹⁴ *Papierfabr.*, 1923, **21**, 89.

²⁹⁵ *J.*, 1923, 294T.

²⁹⁶ *J.*, 1921, 502A, 805A.

²⁹⁷ Offe, *Gas u. Wasserfach*, 1922, **65**, 773; *J.*, 1923, 138A.

²⁹⁸ *Brennstoff-Chem.*, 1923, **4**, 24; *J.*, 1923, 134A; cf. also H. Wolff and C. Dorn, *Farben-Zeit.*, 1922, **28**, 330; *J.*, 1923, 62A.

²⁹⁹ A. E. Dunstan, *J. Inst. Petrol. Tech.*, 1922, **8**, 578; *J.*, 1923, 172A.

and in the absence of standard methods for tar distillates valuable guidance may be obtained in the cases in which the tests are applicable.

The use of alumina as an absorbent for water in organic analysis is recommended by H. L. Fisher, H. L. Faust, and G. H. Walden.³⁰⁰

CALORIMETERS AND OTHER INSTRUMENTS USED IN GAS WORKS.

(By James W. Wood, M.Sc., A.I.C., Research Chemist, Fuel Department, the University, Leeds, and Institution of Gas Engineers.)

The Boys recording gas calorimeter was noted in last year's Report,³⁰¹ and detailed specifications are now available.³⁰² Further improvements were described by Professor C. V. Boys in a lecture at the Royal Institution in April last.³⁰³ So far, however, no specimens of the complete instrument are available for distribution. The Fairweather recording gas calorimeter has been subjected to a practical examination by a Committee of the Institution of Gas Engineers.³⁰⁴ The conditions necessary for the accurate measurement and control of gas by the use of the escapement meter are clearly indicated. The value of an instrument relying upon jet control for the regulation of water supply may be estimated from the Report. It is concluded that, when properly installed, and with occasional skilled attention, the recorder is capable of working continuously with an accuracy of $\pm 0.5\%$ under favourable conditions as to temperature and quality of water supply. J. W. Wood³⁰⁵ gives a critical survey of existing recording calorimeters such as would facilitate selection and operation in particular cases. A "therm meter" is described³⁰⁶ in which the dials indicate therms, adjustment for any predetermined calorific value being made by alteration of the water level in the meter by regulation of overflow level. J. C. Stewart³⁰⁷ describes the "Sigma" calorific value recorder. The same instrument can be adapted as a CO₂-recorder for flue gases if the governors on the gas supply are operated by differences in density between flue-gas and air.

The Beasley recorder³⁰⁸ has been fitted with a device for correcting its readings for variations in atmospheric temperature and pressure.

³⁰⁰ *Ind. Chem. Eng.*, 1922, **14**, 1138; *J.*, 1923, 104A.

³⁰¹ *Ann. Repts.*, 1922, **7**, 64.

³⁰² *Gas J.*, 1923, **162**, 104, 168, 225. E.P. 195,180; *J.*, 1923, 528A.

³⁰³ *Ibid.*, 1923, **162**, 271.

³⁰⁴ *Ibid.*, 1923, **161**, 462, 524, 692, 693, 766; **162**, 30, 106; **163**, 30, 102, 222, 598, 677, 744; *J.*, 1923, 756A.

³⁰⁵ *Ibid.*, **161**, 205.

³⁰⁶ *Ibid.*, **163**, 751.

³⁰⁷ *Ibid.*, **162**, 36.

³⁰⁸ *Ibid.*, **164**, 49. *J.*, 1923, 457T.

A suitably devised brake varies the rate of oscillation of the pendulum controlling the meter.

W. C. Peebles has placed on the market a simple calorific value indicator³⁰⁹ operating by the flexure of a compound metal bar, when heated by a specially controlled Bunsen burner.

Important modifications in the methods officially adopted for the determination of the calorific value of gas will be found in the latest "Notification" of the Gas Referees.³¹⁰

A type of bomb calorimeter has been devised by E. Brown³¹¹ in which the electrodes are arranged so as to suffer the minimum amount of damage during combustion, and the method of closing the bomb is novel. Diffusion through a porous diaphragm and measurement of the consequent pressure difference on its two sides has been applied to gas analysis--mainly flue-gases--in the W.R. CO₂-recorder.³¹²

³⁰⁹ E.P. 203,949; *J.*, 1923, 1108A.

³¹⁰ "General Notification of Gas Referees, June, 1923." H.M. Stationery Office.

³¹¹ E.P. 194,554; *J.*, 1923, 475A.

³¹² *Gas J.*, 1923, 161, 336.

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³⁰⁰ *Ind. Chem. Eng.*, 1922, **14**, 1138; *J.*, 1923, 104A.

³⁰¹ *Ann. Repts.*, 1922, **7**, 64.

³⁰² *Gas J.*, 1923, **162**, 104, 168, 225. E.P. 195,180; *J.*, 1923, 528A.

³⁰³ *Ibid.*, 1923, **162**, 271.

³⁰⁴ *Ibid.*, 1923, **161**, 462, 524, 692, 693, 766; **162**, 30, 106; **163**, 30, 102, 222, 598, 677, 744; *J.*, 1923, 756A.

³⁰⁵ *Ibid.*, **161**, 205.

³⁰⁶ *Ibid.*, **163**, 751.

³⁰⁷ *Ibid.*, **162**, 36.

³⁰⁸ *Ibid.*, **164**, 49. *J.*, 1923, 457T.

within the British Empire. It is understood that the State boring at Roma, Queensland, is to be finally abandoned, after influx of water at high pressure on the gas-bearing stratum caused shutting off. In New Zealand, the boring at New Plymouth has not realised expectations, and operations have been stopped owing to the failure of well casing. The New Plymouth borings had yielded the best flow of oil in New Zealand.

No oil has yet been discovered in South Africa, despite continued search and survey, though recent advices indicate the possibility of its existence in Rhodesia.¹

On the other hand the refining of crude petroleum is rapidly becoming an important industry in the United Kingdom. During the first six months of 1923 over 146 million gallons of crude oil was imported, this being an increase of more than 52 million gallons over the corresponding period for the previous year. It is worthy of note also in emphasising the importance of this modern development that during the same period petroleum products of British manufacture were exported to the value of £1,192,064, this representing an increase in bulk over that of the first six months of 1922 of over 28 million gallons.

Other European countries are also taking great interest in the development of their oil resources, but whether such development is likely to be impeded by the American over-production remains to be seen. Jugo-Slavia has extensive evidence of deposits in old Serbia, and both Bosnia and Montenegro are regarded as potential oil areas.² In Spain the exploitation of the Santander and Alava provinces is looked on hopefully,³ and in Germany the extraction of oil from the Wietze sands, near Hanover, is being carried on by actual mining, the oil being washed out after the sand has been brought to the surface.⁴ In this connexion, also, the report of D. V. Golubianikoff⁵ on the amount of undeveloped oil land in the Baku district indicates the importance attached to the exploitation of their petroleum resources by the Soviet Government. It is estimated that land from which about 1764 million poods (over 28 million tons) per annum could be produced, remains to be developed.

Concerning extra-European enterprises a significant comment is made⁶ to the effect that in view of the over-production in the United States and the continued large production in Mexico, developments by South American oil companies have received a

¹ *Financial News*, Dec. 5, 1923.

² *Oil Weekly*, July 14, 1923.

³ *U.S. Commerce Reports*, July 16, 1923.

⁴ *J. Inst. Petr. Tech.*, 1923, 9, XV.

⁵ *Ibid.*, 185.

⁶ *Wall Street J.*, July 18, 1923.

set-back of several years and that expenditure of money for such developments is not warranted at present.

CRUDE OIL.

In discussing a paper by W. A. Guthrie⁷ on heavy-grade Egyptian crude petroleum, A. E. Dunstan⁸ pleads for the storage for posterity of large samples of the oils from the chief producing fields, since it appears certain that before very long many of these crude oils will not be available for detailed examination. The suggestion seems very cogent, since future technique may bring to light important knowledge on the composition of the heavier fractions of mineral oil, which at present appears unattainable.

THE ORIGIN OF PETROLEUM.

Little original work has been published on this engrossing subject during the past year, but the researches of E. Pyhälä⁹ deserve attention as providing data which are claimed to uphold the theory of the inorganic origin of petroleum. One of the objections to this theory, which has had few adherents of recent years, is the alleged fact that no high-viscosity hydrocarbons of the lubricating oil type have been shown to originate from the products of the action of water on metallic carbides. Working with the unsaturated residues from the separation of light aromatic compounds obtained by cracking Baku petroleum, Pyhälä has shown the polymerisation of the most mobile fractions to oils of high molecular weight, corresponding to spindle, machine, and cylinder oils. This observation is of interest, but its importance would be greater had the unsaturated compounds been obtained in the first place from inorganic sources. R. H. Brownlee¹⁰ has already shown the formation of lubricating oils by the condensation of light unsaturated compounds.

Pyhälä also claims that the slight optical activity of petroleum, which is regarded as proof of its organic origin, may best be explained by the presence of minute traces of accessory substances of vegetable origin.

The inorganic theory of the origin of petroleum receives support from W. Ramsay,¹¹ who comments on the remarkable, almost universal, occurrence of nickel as a constituent of petroleum ash, and draws the conclusion that the catalytic reduction of carbon monoxide or carbon dioxide in the presence of nickel, after the method of Sabatier and Senderens, possibly accounts for most of

⁷ *J. Inst. Petr. Tech.*, 1923, **9**, 212; *J.*, 1923, 964A.

⁸ *Ibid.*, 234.

⁹ *Petroleum*, 1923, **19**, 495, 535; *J.*, 1923, 699A.

¹⁰ U.S.P. 1,309,432; *J.*, 1919, 621A.

¹¹ *J.*, 1923, 287T.

the petroleum deposits. The presence of other catalysts, such as copper and vanadium, is also noted. The possibility of the "poisoning" of the catalysts by sulphur or carbon monoxide is discussed, but it is considered that the catalyst might become re-activated or the conditions under which the formation of petroleum takes place be such that poisoning does not occur. The fact that the more unsaturated petroleums contain least nickel is considered further to support the theory.

A valuable paper by E. H. C. Craig¹² summarises the most important of recent investigations bearing on the origin of petroleum.

ANALYTICAL.

The most important feature of the year in this section has been the completion of the first, and major, report of the Committee appointed by the Institution of Petroleum Technologists in 1921 for the purpose of standardising the analytical tests used in the mineral oil industry,¹³ and of which a critical resumé has already been published by A. E. Dunstan.¹⁴ The Committee has aimed at delivering authoritative decisions on the many points concerning which petroleum technologists have hitherto worked under serious difficulties, owing to the previously existing divergencies in methods and interpretation of results. As far as possible the methods recommended have been chosen to accord with those of the American Society for Testing Materials and the American Bureau of Standards, but in a number of cases, methods generally accepted in British practice have been retained despite the desire to secure world-wide uniformity. Thus, for example, the Abel closed flash test and the Redwood viscosity test are so firmly established that to adopt other standards in their place could only be justified had they serious technical shortcomings, which is certainly not the case.

Besides the standardisation of methods the I.P.T. Committee has concerned itself with the standardisation of apparatus. Indeed, several of their most important recommendations deal with the unexpectedly grave variations which their investigations have revealed in what have been generally regarded as standard instruments. Thus, the dimensions and permissible degrees of tolerance for the apparatus used in the Engler distillation test have been laid down with extreme exactitude, and similar data are given for the first time for the determination of water and sediment by means of the centrifuge. In order to give effect to their recommendations and to secure certification of instruments the Committee has taken the important step of arranging with the National Physical

¹² *J. Inst. Petr. Tech.*, 1923, **9**, 344.

¹³ *Ibid.*, 1923, **9** (advance proof).

¹⁴ *Ibid.*, 1922, **8**, 578; *J.*, 1923, 172A.

Laboratory for the calibration, testing, and making of instruments complying with the adopted standards.

It is manifestly impossible to discuss this important and useful report in any detail, since it covers nearly all the principal mineral oil tests, leaving only minor tests for future consideration, but it is of interest to note that the lamp method for the determination of sulphur has been made standard and that an exact method for determining the sludging values of transformer and switch oils has been laid down. The work reflects great credit on the Institution of Petroleum Technologists.

A serious difficulty with regard to standard tests has been pointed out by P. E. Klopsteg and W. H. Staniford.¹⁵ For measuring viscosities on the Saybolt instrument the A.S.T.M. specify a degree of constancy in the temperature of the bath of 0·25° F., and the authors assert that it is quite impossible to comply with this requirement while stirring by hand and with the usual type of thermo-regulator. They have consequently devised an electrical heating regulator which, in combination with a special stirring arrangement, meets the requirements of the test.

Regarding the interesting problem of the separation of the components of petroleum, more work has been done by P. F. Gordon.¹⁶ His preliminary communication contains a critical examination of the industrial methods of separation of products from Burmah crude oil, giving comprehensive details, in chart form, of the process used with ordinary works plant, and directs attention to the inefficiency of certain refining methods.

The physical condition of crude oil is discussed and experimental work on fractional precipitation, emulsification, and surface tension has been started and preliminary results are recorded in detail.

Some components of crude oil exist in the colloidal condition, but ordinary methods for coagulating colloids do not effect separation. Solid paraffin wax can be separated from crude oil by precipitation, so that the existence of so-called proto-paraffin is not essential to account for the behaviour of solid paraffins in undistilled oil. Crude petroleum may be fractionally precipitated from a suitable solvent and fractions thus obtained from Hardstoft crude do not show the same gradation in viscosity as distillates. Higher fractions from petroleum behave as emulsoids and do not contain a higher percentage of unsaturated compounds than lower fractions.

A higher hydrocarbon in solution in a lower one lowers the surface tension of the latter, and the surface tension of fractions from crude oil decreases as the specific gravity rises. The surface tension of a light fraction is lowered by the addition of a higher fraction, but a mixture of light and heavy fractions may have a lower surface

¹⁵ *Ind. Eng. Chem.*, 1923, 15, 702; *J.*, 1923, 866A.

¹⁶ *J.*, 1923, 405T.

tension than either of the components. The surface tension of pure hydrocarbons and the best conditions for separating components of a mixture of hydrocarbons at surfaces, are being determined.

The necessity for preparing pure hydrocarbons led to the investigation of known methods of preparation, but the inefficiency of these caused the return to petroleum as the starting point, and fractions from Anglo-Persian crude oil were brominated by Herzfelder's method, yielding colourless crystalline compounds, the separation of which in the pure state was comparatively simple.

W. R. Ormapddy and E. C. Craven¹⁷ have continued their work on the effect of varying conditions on flash-point determination and have endeavoured to find some physico-chemical significance of the test. With this point in view they have investigated the effect on flash-point temperatures of reduced and increased pressures, of altering the composition of the atmosphere, and of temperature of the vapour-air mixtures. Certain empirical relationships are given, but it seems questionable whether "flash point" can in any sense be regarded as a true physical constant and, therefore, capable of the interpretation the authors seek.

The vexed question of the determination of iodine values of petroleum oils has been re-investigated by S. Kawai,¹⁸ who emphasises the fact that whatever method is adopted the exact conditions must be specified if results are to be at all comparable.

The well-known American "doctor" test for sulphur in motor fuels is again the subject of adverse criticism, and J. C. Chatfield¹⁹ points out that elemental sulphur, which may be very detrimental to motor spirit, cannot be detected by the doctor test. Similar conclusions are come to by J. V. Meigs and E. J. Ford.²⁰ For nearly every reason the importance hitherto attached to this test seems very undesirable. For the rapid determination of water in mineral oils L. Losana²¹ has devised a method which appears to give good results and is based on the measurement of the increase of pressure or of the volume of hydrogen evolved when the oil is agitated with calcium or sodium amalgam.

L. C. Kerrick and V. F. Parry²² overcome the difficulties of determining the melting points of greases and the like by spreading the grease on an electrically heated rod with constant temperature differences between the two ends, and observing the point at which adhesion commences when a blast of air is moved at a fixed rate along the rod. The melting points determined by this novel method are stated to be quite sharp.

¹⁷ *J. Inst. Petr. Tech.*, 1923, **9**, 33; *J.*, 1923, 173A.

¹⁸ *J. Chem. Ind. Japan*, 1922, **25**, 406.

¹⁹ *Nat. Petr. News*, Nov. 15, 133.

²⁰ *Refiner*, 1923, **2**, 6.

²¹ *Giorn. Chim. Ind. Applic.*, 1923, **4**, 570; *J.*, 1923, 172A.

²² *Ind. Eng. Chem.*, 1923, **15**, 600; *J.*, 1923, 700A.

CRACKING.

Probably the most striking advance in petroleum technology during 1923 has been the steady development of so-called liquid-phase processes for the production of light spirit by the thermal decomposition of heavy oils.

Attention has been drawn to some of these processes in previous reports, but the facts that G. Egloff and J. C. Morrell²³ estimate the 1923 production of cracked gasoline in the United States of America as approximately 2800 millions of gallons, and that much the biggest proportion of this is produced by liquid-phase processes, indicate the industrial importance of the subject.

The processes of R. Cross,²⁴ C. Ellis²⁵ (Standard Oil Company), J. C. Black,²⁶ S. J. M. Auld, A. E. Dunstan, and P. H. Herring,²⁷ and others are directed towards the substantial maintenance of the liquid state during the thermal decomposition of the heavy oils and the deposition of the carbon necessarily formed during the process, in special settling chambers which are not strongly fired or from which heat loss is reduced to a minimum by heavy lagging. The processes differ in the attainment of these conditions, and in the newer process of Auld, Dunstan, and Herring, in which there are three distinct zones of heating, no decomposition takes place in the firing chamber.²⁸

Besides these liquid-phase processes, further development of the pressure distillation method of cracking has occurred through the application of the Dubbs patent²⁹ to the decomposition of heavy oils. This patent, which was obviously originally intended to deal with the dehydration of emulsified oils, has been broadened in such a way as to admit of the treatment of hydrocarbon oils under heat and autogenous pressure applied both to stills and condensers. It has thus become a serious competitor of the Burton pressure distillation process, and has the advantage over the latter that the still is not directly fired, but receives its heat from the incoming oil, which itself is heated in coils suitably disposed in a furnace.

Extensive litigation was threatened in America between the controllers of the Cross and Ellis processes on the one hand and between the Dubbs and Burton processes on the other hand, but differences have apparently been settled by agreement and all four methods are now in vogue, though the Burton process would now appear obsolescent.

²³ *Chem. and Met. Eng.*, 1923, **29**, 53; *J.*, 1923, 757A.

²⁴ U.S.P. 1,437,229; *J.*, 1923, 87A.

²⁵ E.P. 174,089; *J.*, 1923, 593A.

²⁶ U.S.P. 1,456,419; *J.*, 1923, 643A.

²⁷ E.P. Appl. 4924, 1923.

²⁸ U.S.P. 1,123,502.

The liquid-phase²⁹ cracking processes possess many advantages over the older vapour-phase processes. They can deal with much heavier cracking stock, even to the extent of cracking fuel oil and heavy Mexican crude oil,³⁰ they produce much smaller proportions of uncondensable gas and carbon, and the light spirit is of very superior quality and easily refined. The refining consists generally of limited acid treatment, followed by a desulphurising process, and is completed by a steam distillation.

Considerable publicity has been given to a cracking process devised by V. L. Emerson,³¹ who advances the novel claim that cracking is caused, or assisted, by the impact of the hydrocarbon molecules when the oil to be cracked is injected at high pressure into an expansion chamber suitably heated. In practice opposed pairs of jets are used, the velocity of the vapours at the jets being approximately 2900 feet per second. Much has been written in support of this "impact process," but it remains to be seen whether it will have any special utility, or whether there is any real basis for the underlying feature of molecular impact.

As usual, a large number of patents dealing with cracking have been granted during the year, of which it is difficult to determine the trend or which are apparently aimed at simulating or extending known processes by the introduction of novel features alleged to be improvements. Most of these have been directed to the development of pressure distillation processes, the older vapour-phase methods being at present somewhat in disrepute.

Apart from such claims, one or two new processes deserve notice by virtue of their unusual character. E. M. Hyatt,³² for example, cracks fuel oil, kerosene, or other hydrocarbons after treatment with chlorine, this gas being passed direct to the pressure still in the proportion of 1-10 lb. per 50 gallons of oil. The gasoline distillate only requires treatment with caustic soda.

Plausons³³ have embodied the use of zinc chloride, alone or mixed with quicklime, in a process for cracking shale or petroleum oils, and the results are stated to be particularly good. Anhydrous zinc chloride, like aluminium chloride, is known to be an excellent refining agent for cracked spirit, but so far has not been found capable of replacing the latter as a "catalyst" for cracking purposes.

No further developments have been recorded of the Bergius process for the direct hydrogenation of oil and coal at high pressures, but a useful review of the subject in its relationship to the production of motor spirit has been published by H. G. Shatwell³⁴ and

²⁹ Cf. G. Egloff, *Nat. Pet. News*, 1923, 15, 12; *J.*, 1923, 699A.

³⁰ E.P. 163,277 and 168,573; *J.*, 1923, 540A.

³¹ U.S.P. 1,445,688; *J.*, 1923, 393A.

³² E.P. 193,071; *J.*, 1923, 593A.

³³ *Fuel*, 1923, 2, 229; *J.*, 1923, 757A.

should be consulted by those interested. H. I. Waterman and N. J. Porquin³⁴ consider the Bergius method to be superior to cracking without hydrogen under pressure.

T. Ulke³⁵ has patented an adaptation of the Bergius process in which the carbonaceous material is hydrogenated by means of sodium formate, or the like, which produces hydrogen at high temperatures, and H. Nielson and B. Laing³⁶ for the same purpose have devised improved catalytic methods for the manufacture of formic acid and its salts.

M. Melamid³⁷ in a series of patents elaborates a process for using tin and other alloys to assist the hydrogenation of hydrocarbons at high temperatures. Atmospheric pressures are employed and, as a rule, temperatures of 600°-800° C. At 900° C. the use of extraneous hydrogen is stated to be unnecessary. The process is claimed to be very promising, but so far does not appear to have reached the large-scale stage.

So many extravagant claims have been made on behalf of cracking processes based on the effects of both high- and low-frequency discharges on petroleum hydrocarbons, that an authoritative paper on the subject by J. J. Jakosky,³⁸ of the U.S. Bureau of Mines, read before the Petroleum Division of the American Chemical Society, is sincerely to be welcomed. Jakosky's work shows clearly that claims as to no carbon formation, polymerisation of uncondensable gas, loss unsaturation, etc., cannot be confirmed and that any other special effects can be reproduced by using a higher temperature in the cracking zone. No hydrogenation could be obtained and the commercial application of the corona discharge seems neither desirable nor feasible.

DISTILLATION AND REFINING.

Emulsions.

The treatment of oil-field emulsions has always been a difficult problem and one which, despite the successful application of centrifugal methods, has not been entirely solved. Electrical dehydrators of various types continue to be evolved. H. C. Eddy,³⁹ using plate electrodes, varies the field automatically as required by means of an electromagnetic device operating on the upper electrode whenever the current exceeds a predetermined value. F. W.

³⁴ Proc. K. Akad. Wetensch., 1923, 26, 226; J., 1923, 757A.

³⁵ U.S.P. 1,445,423; J., 1923, 302A.

³⁶ E.P. 198,385; J., 1923, 760A.

³⁷ E.P. 171,367, 171,390, 174,321, 180,625, 193,922; J., 1923, 259A, 393A.

³⁸ J. Inst. Pet. Tech., 1923, 9, 266A.

³⁹ U.S.P. 1,442,808; J., 1923, 259A.

Harris⁴⁰ employs rotating electrodes and also an annular arrangement intended to maintain a field of uniform thickness. In another modification⁴¹ of his process, plate electrodes are used and the upper electrode is insulated.

Refinery emulsions may come under the same general treatment as crude oil emulsions, but for various reasons gravity or centrifugal separation of the water is more desirable. H. V. Dodd⁴² points out that in petroleum emulsions asphalt is most frequently the emulsifying agent and that separation may be effected by attacking the emulsifying agent or by increasing the surface tension of the interface. By the addition of electrolytes having strongly adsorbed positive ions, emulsions may be broken by neutralising the negative charges carried by the dispersed water globules, providing that the electrolyte can be conveyed through the oil envelope to the dispersed water. For the purpose, it is necessary to use a substance partially soluble in both phases, and Dodd has found acidified phenol to be very efficacious. Phenol added to kerosene-acid-sludge acts even better. Very small quantities of acid only are necessary, so that injury to plant is unlikely. H. A. Gil⁴³ recommends the addition to the emulsion of small quantities of a colloid soluble in water, as for example glue, the addition of which in the proportion of 0.1% is claimed to render the emulsion amenable to centrifugal treatment. For a similar purpose E. E. Ayres⁴⁴ uses solutions of sodium resinate in liquids miscible with petroleum.

Distillation.

Apart from the design of vertical topping stills, several types of which are now in continuous use, and of distillation assemblies for the purpose of producing special cuts, there have been few advances in plant design for petroleum distillation for many years. The bulk of the world's petroleum continues to be distilled from ordinary cylindrical stills. E. H. Leslie,⁴⁵ in his recently published book, ascribes this fact to the general utility of the cylindrical still in comparison with its only serious competitor, the pipe still. The latter is undoubtedly a more intelligently designed plant, but the boiler type of still is more flexible and can be built of smaller capacity without much loss of efficiency. Leslie regards the modern pipe still in its elaborated and refined design as distinctly the plant for the large company.

⁴⁰ U.S.P. 1,440,828 and 1,455,139; *J.*, 1923, 217A, 705A.

⁴¹ U.S.P. 1,458,291; *J.*, 1923, 818A.

⁴² *Chem. and Met. Eng.*, 1923, 28, 249; *J.*, 1923, 299A.

⁴³ E.P. 195,876; *J.*, 1923, 541A.

⁴⁴ U.S.P. 1,454,816-7; *J.*, 1923, 594A.

⁴⁵ "Motor Fuels" (Chemical Catalog Company, 1923).

A form of pipe still in which the oil is heated by hot gases passing in a counter-current direction has been devised and patented by the Stirling Boiler Company and W. W. Wait.⁴⁶

In discussing the operation of stills fitted with columns, F. H. Rhodes,⁴⁷ in an interesting paper, advocates the use of single condensation as against "partial condensation," i.e., dephlegmation. This, of course, is a matter of considerable importance as being opposed to existing theory and practice, but Rhodes claims that simple columns can be more advantageously applied to the distillation of high-boiling liquids and that the operation requires a minimum of attention. This may be true of intermittent distillation, but it scarcely seems to accord with known practice for continuous stills. To make up for the loss of heavy reflow to the column where dephlegmators are used, Rhodes recommends the addition of further plates to the simple columns.

Valuable information of assistance in refinery practice is given by J. C. Morrell and G. Egloff,⁴⁸ who compared the results of distillation under atmospheric and reduced pressures of a number of American crude oils. With the exception of Mexican crude oil, the percentage of unsaturated compounds produced is lower during the reduced pressure distillations. Although the same yield of lubricating oil stock was obtained, the low-pressure distillation product had much higher viscosity than that obtained by distillation at atmospheric pressure and the yield of wax was increased. Less cracking takes place under reduced pressure than at atmospheric pressure, and this accounts for the marked difference in the products obtained.

The Griscom-Russell Co.⁴⁹ has patented a fractionating column containing a large number of vertical tubes and with the upper or dephlegmating portion cooled by a medium, which takes a tortuous path directed by a helical baffle.

Refining Agents.

Experiments conducted by H. I. Waterman and D. W. Sissingh⁵⁰ on the desulphurisation of asphaltic Mexican crude oil have shown that acid washing followed by soda treatment is quite efficient for the purpose. Sodium plumbite appears to have no advantage over caustic soda, whilst the common practice of adding flowers of sulphur is actually harmful. P. von Ditmar⁵¹ desulphurises hydrocarbon oils successfully by digestion with the metallic soaps of the

⁴⁶ E.P. 191,465; *J.*, 1923, 216A.

⁴⁷ *Chem. and Met. Eng.*, 1923, 28, 290.

⁴⁸ *J.*, 1923, 188T.

⁴⁹ E.P. 174,569; *J.*, 1923, 440A.

⁵⁰ *Chem. Weekblad*, 1922, 18, 489; *J.*, 1923, 5A.

⁵¹ U.S.P. 1,448,643; *J.*, 1923, 441A.

higher fatty acids, N. H. Freeman⁵² desulphurises oils in an atomised form, for example, with ammonia, and A. C. Nesfield⁵³ removes sulphur compounds by successive treatment with hydrochloric acid gas mixed with air, and caustic soda.

For the purification of petroleum products, particularly for desulphurising and decolorising, many naturally occurring earths have been employed, and of late years the Death Valley clay of California has found much technical application.

According to H. L. Kaufmann,⁵⁴ halloysite, pyrophyllite, and montmorillonite are all useful for the purpose, the last named having twice the efficiency of the other two. Death Valley clay is of the first type. The clays are digested with weak acid and are merely air-dried, as the presence of water is advantageous since it promotes agitation by the disengagement of steam. The treatment is carried out at 120°–175° C. C. Cramer⁵⁵ has prepared earths, having excellent decolorising properties, by emulsifying aluminium hydrosilicates with dilute hydrochloric acid at ordinary temperatures. M. A. Rakusin⁵⁶ has investigated the limits of adsorptive power of floridin for decolorising petroleum oils, and finds that the effect of time of contact is much more marked than the effect of quantity. A. E. Dunstan and F. G. P. Remfry⁵⁷ find it advantageous to use floridin or fuller's earth and bauxite or similar substances in succession in the treatment of kerosene for the removal of colour and sulphur. This appears sound, for surfaces capable of adsorbing colour efficiently have not the same capacity for removing other types of dissolved matter.

E. Zerner, H. Weiss, and H. Opalski⁵⁸ have determined the mutual solubilities of many hydrocarbons and liquid sulphur dioxide. They find that the solubility curves of all the substances used, e.g., toluene, *n*-tetradecane, *n*-pentatriacontane, deca- and tetrahydronaphthalene, show well-defined maxima. In general, the paraffins are the least soluble, the naphthenes more so, and the aromatic and unsaturated compounds are easily soluble. The solubility decreases with increase of molecular weight.

C. R. Ehlers⁵⁹ claims that aromatic amines, e.g., aniline, toluidine, etc., are suitable agents for purifying mineral oils by virtue of their capacity for removing resinous, tarry, and bituminous substances when agitated with the oils in the proportion of 30–70%.

⁵² E.P. 193,979; *J.*, 1923, 487A.

⁵³ E.P. 196,680; *J.*, 1923, 593A.

⁵⁴ *Nat. Petr. News*, 1923, **15**, 81.

⁵⁵ U.S.P. 1,455,955; *J.*, 1923, 643A.

⁵⁶ *Petroleum*, 1922, **18**, 797.

⁵⁷ E.P. 190,553; *J.*, 1923, 174A.

⁵⁸ *Z. angew. Chem.*, 1922, **35**, 253; *J.*, 1922, 581A.

⁵⁹ E.P. 184,091; *J.*, 1922, 802A.

GUM-FORMING SUBSTANCES.

A comprehensive report on the gum-forming constituents of gasoline has been published by N. A. C. Smith and M. B. Cooke,⁶⁰ of the U.S. Bureau of Mines. They state that no direct connexion appears to exist between gum formation and the unsaturated hydrocarbon content. On the other hand they consider the formation of aldehydes by oxidation of certain unsaturated hydrocarbons to be a probable explanation of the presence of gumming substances in gasoline. As all tests applied for the detection of phenols were negative, the possibility of the gums being phenol-aldehyde condensation products was dismissed, though the behaviour and analysis of the gum suggested this hypothesis. Smith and Cooke regard the well-known copper dish test for gumming as thoroughly unsatisfactory, and recommend the adoption in its place of a simple standardised process based on evaporation from glass dishes and drying the gum at an elevated temperature. The unsatisfactory nature of the copper dish test has also been pointed out by J. V. Meigs and E. J. Ford,⁶¹ who suggest the use of a glass dish containing metal turnings when gum deposition and actual corrosion are to be distinguished.

MOTOR FUELS.

Two factors bear in a most important way on the search for new fuels for internal combustion engines. The first is the natural tendency on the part of automobile engineers to increase efficiency by increasing the compression ratio, which leads to higher thermal efficiency, and the second is the deep-rooted feeling that despite periods of over-production the world's supplies of petroleum will before long be insufficient to meet the increasing demand. These factors are closely inter-related, for no petrol will bear a compression in the neighbourhood of only 4·5 : 1 without excessive detonation in the combustion chamber, an effect which H. R. Ricardo⁶² has established as producing the metallic sound known as "pinking," and the heavier the petroleum product the lower is the maximum compression ratio which can be used. On the one hand, therefore, there is a search for new high-compression fuels which will open up fresh sources of supply, and on the other the search for materials capable of reducing detonation and the admixture of which in small quantities will allow of the use of petrol and also of kerosene in high-compression engines.

Under the first heading comes the work on the utilisation of alcohol and mixtures containing alcohol and the related investi-

⁶⁰ U.S. Bureau of Mines Report No. 2394, 1922.

⁶¹ Refiner, 1923, 2, 6.

⁶² Aut. Eng., 1921, 11, 51, 92, 130, 169.

gations into the value of aromatic compounds as "anti-knocks." Ricardo gave the following useful table of "highest useful compression ratios" showing the value of these materials : Petrol, 4·5 : 1 to 6·0 : 1 ; benzene (98%), 6·9 : 1 ; toluene and xylene, 7·0 : 1 ; alcohol (98%), 7·0 : 1.

Since the publication of the last Annual Reports further developments in the investigation of detonation have been made by T. Midgley.⁶³ According to Midgley "pinking" is due to a high-pressure high-velocity wave striking the cylinder walls. In any explosive wave a difference of pressure exists between the front and rear of the wave, and above a certain critical pressure in the rear this pressure difference becomes very great, the explosion becomes a detonating one, and knocking is caused. Midgley's "anti-knocks," such as diethyl selenide and tetra-ethyl lead,⁶⁴ act by reducing the velocity of combustion, and except that the materials are not unchanged at the end of the action, appear to act catalytically. The property of retarding knocking appears to be a function of the element rather than that of the groups attached to it, though the attached radicles have modifying effects. In distinction from the anti-knocks there are substances which induce knocking, the alkyl nitrates and nitrites being especially active in this way.

Attention has been paid by J. H. James and F. C. Zeisenheim⁶⁵ to the use as fuel of oxidised kerosenes and similar products. These oxidised fuels are believed to undergo particularly good combustion, and they show lower detonation tendencies than straight hydrocarbon fuel. On the other hand they gave heavy yields of gum, but this gum is mostly in the fraction boiling above 300° C. The experimenters claim that the oxidised fuels are eminently suitable for kerosene engines and for blending with petrol.

Development of the use of alcohol as a fuel, either alone or blended with other materials, is reviewed in other sections of these reports.

As far as blends with petrol or other mineral oil fractions come under discussion little progress has been made during the year, the chief point being the continued search for suitable agents to aid the miscibility of petrol and 95% alcohol. No striking discoveries have been made up to the present. W. R. Ormandy and E. C. Craven⁶⁶ suggest a means for expressing the mixing value of different substances in terms of the change of separation point, the quantity of mixer added, and the volume of alcohol.

⁶³ *Nat. Petr. News*, 1922, 59 ; *J. Ind. Eng. Chem.*, 1922, **14**, 589, 894 ; *Ind. Eng. Chem.*, 1923, **15**, 421.

⁶⁴ Cf. *Ann. Repts.*, 1922, 7, 80.

⁶⁵ *Chem. and Met. Eng.*, 1923, **28**, 543 ; *J.*, 1923, 391A.

⁶⁶ *J. Inst. Pet. Tech.*, 1923, **9**, 129 ; *J.*, 1923, 592A.

A comprehensive paper read by H. Moore⁶⁷ deals with most of the difficulties encountered in burning heavy fuels in heavy-oil engines, and should be consulted by those interested.

LUBRICANTS AND LUBRICATION.

T. E. Stanton,⁶⁸ in an interesting paper read before the International Air Congress, London, 1923, discusses the nature of lubrication in engineering practice. There are two essentially different kinds of lubrication, that known as the Reynolds type in which the film of lubricant is hundreds of molecules thick, and that termed by W. B. Hardy "boundary" lubrication, in which lubrication is a function of the nature of the surfaces and the chemical constitution of the lubricant. The scientific and economic importance of the investigation of boundary lubrication is obvious. For this purpose Stanton has used an apparatus in which the experimental bearing is contained in a housing suspended pendulum-wise in such a manner as to allow adjustment in a direction at right angles to the plane of the swing. Pressures are thus symmetrical on either side of the plane of oscillation. The total arc of contact is 45° on either side, and to approximate to the supply of lubricant to a worm gear special grooves are cut in the 90° arc of the bearing and similar grooves at right angles to them on the surface of the journal. The results of Stanton's experiments show that with the pendulum apparatus the characteristics of lubricants can be investigated rapidly and conveniently. An important conclusion is that the lubrication of all details in which the relative motion is reciprocatory is of the boundary type, and efficiency in lubrication may therefore be looked for in the direction of altered chemical composition. All recent work tends to confirm this view on the dependence of lubrication on physico-chemical considerations.

A. E. Dunstan and F. B. Thole⁶⁹ are of the opinion that the property of "oiliness" in mineral oil lubricants is due to the reactive unsaturated constituents which act by entering into physico-chemical union with the solid faces lubricated, forming new composite surfaces of lower surface energy and thus opposing less resistance to shear. This is fully in accord with Hardy's views, and is confirmed by the great activity of free fatty acids in increasing the lubricating value of mineral oils.

In order to make the results of tests of "oiliness" carried out on friction-testing machines more intelligible and of general application, W. H. Herschel⁷⁰ recommends the adoption of the method of

⁶⁷ *J.*, 1923, 134A.

⁶⁸ *J. Inst. Pet. Tech.*, 1923, 9, 260.

⁶⁹ *Chem. and Met. Eng.*, 1923, 28, 299.

⁷⁰ *Ibid.*, 1923, 28, 302.

reporting tests in use at the Bureau of Standards, Washington. Replacing in Sommerfeld's equation Δ , the film thickness of a concentric journal, by 2Δ , the difference in diameter between bearing and journal, Herschel obtains what he calls Sommerfeld's criterion $\frac{\eta n}{p} \left(\frac{d}{2\Delta}\right)^2$ which thus takes into account the eccentricity

of a journal in its bearing. Herschel recommends that the viscosity η should be taken in poises, p in dynes per square centimetre, and d and Δ in any convenient unit. When the clearance is unknown $2\Delta/d$ should be taken as 0.001, a not unusual value. Using this method with a friction-testing machine of the Cornell type, Herschel⁷¹ comes to the conclusion that the material and smoothness of the bearing and journal have a greater influence than the nature of the lubricant and that journal friction-testing machines are not convenient for testing oiliness owing to the change of clearance with wear.

M. D. Hersey⁷² describes experiments on the important subject of the viscosity of lubricants at high pressures and temperatures. The apparatus employed was a rolling-ball viscometer modified for use at high pressures. At low temperatures the viscosity curves for mineral oils ascend very steeply all the way, whereas with fixed oils there is a preliminary gradual slope. At 100° C. both classes show a more gradual increase.

In the manufacture of lubricating oils the use of high-speed centrifugal separators for removing wax continues to find favour and is strongly advocated by L. C. Welch.⁷³ The Sharples Company⁷⁴ continue to improve their processes for this purpose. J. Marcusson and F. Böttger⁷⁵ show that lubricating oils may be prepared from lignite tars by condensation with zinc chloride or by heating under pressure, but the oils obtained rapidly fall off in viscosity with increase of temperature, and have high saponification and iodine values.

The necessity of maintaining a high standard for transformer oils is well known, and F. Schwarz and J. Marcusson⁷⁶ recommend as a test for these oils a modification of Holde's determination of the "tar number," which is the amount of material extractable by alcoholic caustic soda solution after subjecting the oil to a period of 50 hours' heating at 150° C. E. Casimir⁷⁷ supports the value of

⁷¹ *Chem. and Met. Eng.*, 1923, **28**, 594; *J.*, 1923, 539A.

⁷² *J. Inst. Pet. Tech.*, 1923, **9**, 218A.

⁷³ *Ibid.*, 1923, **9**, 95A.

⁷⁴ E.P. 191,750; *J.*, 1923, 703A.

⁷⁵ *Mitt. Materialprüf.*, 1922, **40**, 250; *J.*, 1923, 300A.

⁷⁶ *Petroleum*, 1922, **18**, 741.

⁷⁷ *Ibid.*, 1923, **19**, 763; *J.*, 1923, 878A.

this test. G. Brühlmann⁷⁸ discusses the adoption of a new "solidifying point" test for transformer oils. In this connexion it is to be noted that the British Electrical and Allied Industries Research Association⁷⁹ in their report consider the existing Michie and B. T. H. evaporation tests and the Archbutt cold test satisfactory.

G. L. Oliensis⁸⁰ has investigated current "demulsibility" tests and considers the vacuum steam test and the more precise Conradson test as suitable for detecting the presence of substances which would be liable to promote breakdown of lubricating oils under practical conditions.

R. E. Wilson and E. P. Wylde⁸¹ have investigated the behaviour of solutions of lubricating oils and volatile solvents and classified the oils chosen according to their tendency to absorb benzene, hexane, and cyclohexane. The results obtained have obvious important practical bearing.

WAX.

F. Francis, G. M. Watkins, and R. W. Wallington⁸² continue their studies of paraffin wax, and have separated from a particular wax of Scottish origin seven fractions of melting point varying from 44·9° to 66·6 C. and molecular weight rising from 325 to 434, which they consider to be pure hydrocarbons. A. Grün and E. Ulbrich⁸³ have obtained increased yields of insoluble fatty acids from 36·5% to 61·7% by passing very large volumes of air (1200 litres per hour) through molten paraffin wax. Apart from these investigations little has been done towards elucidating the composition of paraffin wax or studying its possible chemical transformations.

It is a well-known fact that the presence of colloidal solids, and particularly of asphaltic substances, seriously hinders the separation of crystalline paraffin wax from heavy oil fractions. The presence of even small quantities of protective colloids also impairs the efficiency of the sweating process for purifying paraffin scale. For the purpose of overcoming these difficulties C. F. Kennedy⁸⁴ and T. C. Delbridge⁸⁵ recommend washing with soap solution the wax-containing oil and the wax previous to sweating respectively. By these means the wax is more easily separated and the crystals obtained are larger and more uniform.

⁷⁸ *Petroleum*, 1923, **19**, 69; *J.*, 1923, 299A.

⁷⁹ *J. Inst. Elect. Eng.*, 1923, **61**, 661.

⁸⁰ *Ind. Eng. Chem.*, 1923, **15**, 690; *J.*, 1923, 816A.

⁸¹ *Ibid.*, 1923, **15**, 801; *J.*, 1923, 1005A.

⁸² *Chem. Soc. Trans.*, 1922, **128**, 2804; *J.*, 1923, 173A.

⁸³ *Z. angew. Chem.*, 1923, **36**, 125; *J.*, 1923, 299A.

⁸⁴ U.S.P. 1,439,171; *J.*, 1923, 216A.

⁸⁵ U.S.P. 1,438,985; *J.*, 1923, 216A.

H. Stinnes⁸⁶ obtains stable wax-like substances from crude montan wax, which normally is dark coloured and brittle, by chlorination, either direct in dilute alkaline medium or by means of hydrochloric acid and potassium chlorate.

NATURAL GAS.

Each year continues to see considerable growth of the exploitation of natural gas, and it is particularly significant that more and more attention is being paid to the possibility of utilising natural-gas hydrocarbons for the production of new products. In the meantime the most important developments are still connected with stripping gasoline from the gas, and according to I. R. C. Cantelo⁸⁷ poor gases containing as little as a quart of recoverable gasoline per 1000 cub. ft. are being successfully treated. Most of the gasoline recovery in the U.S.A. is now carried out on a large scale, and E. G. Sievers⁸⁸ states that the majority of the small plants are being consolidated, as it is hardly profitable to produce less than 1000 gallons of gasoline per day in a single plant.

Burrell's method of stripping natural gas with the aid of activated charcoal continues to find favour. W. Friedmann⁸⁹ and Meister, Lucius, und Brüning⁹⁰ have devised a continuous plant for the purpose which avoids the need of removing the charcoal for revivification. Most of the natural-gas gasoline, however, is still obtained by compression methods, though a combination of liquid absorption and compression is now coming into favour.⁹¹ Amongst the improvements in the liquid absorption process may be mentioned that of E. A. Starke,⁹² who obtains intimate contact by passing both gas and oil into the suction side of a centrifugal pump, and those of C. C. Reed⁹³ and E. S. Merriam,⁹⁴ who attempt to make the process continuous.

Natural-gas gasoline tends rapidly to go off colour and become sour, and D. B. Dow,⁹⁵ in a description of known methods of purifying this gasoline, lays considerable weight on the value of the caustic soda solution of litharge known as "doctor" solution.

In the Rivadavia field W. Friedmann⁹⁶ has attempted to utilise waste natural gas in place of steam for distillation purposes, and has

⁸⁶ E.P. 199,073; *J.*, 1923, 818A.

⁸⁷ *Can. Chem. and Met.*, 1922, 6, 177, 196.

⁸⁸ *Chem. and Met. Eng.*, 1923, 28, 297.

⁸⁹ *Petroleum*, 1923, 19, 367; *J.*, 1923, 538A.

⁹⁰ E.P. 187,223; *J.*, 1923, 386A.

⁹¹ Sievers, *loc. cit.*

⁹² U.S.P. 1,439,921; *J.*, 1923, 704A.

⁹³ U.S.P. 1,456,570; *J.*, 1923, 704A.

⁹⁴ U.S.P. 1,457,780; *J.*, 1923, 704A.

⁹⁵ *Nat. Pet. News*, 1923, 15, 99.

⁹⁶ U.S.P. 1,456,570; *J.*, 1923, 704A.

had successful results in treating strongly emulsified oils by its aid. These oils, containing 30% of water, are otherwise undistillable.

Though it is true that more and more attention is being paid to the utilisation of oil-field gas, there is in many fields an inordinate production of gas, and this leads inevitably to an unnecessarily rapid exhaustion of the petroleum-bearing strata. To the loss of pressure in the wells due to this cause J. Strijow⁹⁷ ascribes the diminished production or exhaustion of many of the Grozni strata, and the same thing applies in many other fields. It is obvious that steps will have to be taken to prevent the free escape of gas or to return it to the producing strata.⁹⁸

The U.S. Bureau of Mines has carried out large-scale experiments on the use of highly volatile natural-gas gasoline as a refinery refrigerant for cooling wax distillates. L. D. Wyant⁹⁹ gives a working description of the plant, which appears to offer considerable promise of providing a cheap and in many cases readily obtainable cooling medium in place of the usual ammonia or carbon dioxide. The only disadvantage is the risk of fire, which, however, should not be great.

The use of highly volatile hydrocarbons for this purpose is not a novelty. According to J. Bryson and Thompson¹⁰⁰ this method was in use in the Scottish refineries over fifty years ago and in 1881-4 was common practice in Scotland, spirit of sp. gr. 0.66 being successfully used.

He'ium in Natural Gas.

According to J. C. McLennan¹⁰¹ the production of helium from natural gas in the U.S.A. amounts to 30,000 to 40,000 cubic feet daily. Of the natural gases within the British Empire, those from Ontario and Alberta are richest in helium with about 0.3%, while the helium content of the Heathfield, Sussex, gas is 0.2% and that from Bath springs 0.15%. In Texas gases are known which contain 1-2% of helium. Helium is particularly suited for filling air-ship envelopes, as it is non-inflammable and has a lifting power only 8% lower than that of hydrogen. It can be mixed with hydrogen to the extent of 15% without the mixture becoming explosive.

Other Constituents of Natural Gas.

Although commercial processes for the production of products such as methyl alcohol and its derivatives from methane are still

⁹⁷ *Grozni pet. Ind.*, 1923, **5-8**, 6; *J.I.P.T.*, 1923, **9**, 272A.

⁹⁸ Cf. A. B. Thompson, "Oil Field Waste," *J. Inst. Pet. Tech.* 1923, **9**, 314.

⁹⁹ *Nat. Petr. News*, 1923, **15**, 99.

¹⁰⁰ Private conversation, 1923.

¹⁰¹ *British Science Guild pamphlet*. 1923.

wanting, much work continues to be done on the subject. T. S. Wheeler and E. W. Blair¹⁰² have proceeded with investigation on the oxidation of hydrocarbons, particularly with a view of obtaining formaldehyde from methane. They show that slow oxidation and a short time of heating are the chief factors in obtaining a good yield of formaldehyde. A. Schleede and C. Luckow¹⁰³ have published a detailed study of the chlorination of methane, when the two gases are passed through electrically-heated quartz tubes. Direct chlorination to methyl chloride, without the formation of higher chlorides, may, indeed, be regarded as successfully accomplished,¹⁰⁴ and attention is now being turned to the replacement of the chlorine by hydroxyl. R. H. McKee and S. P. Burke¹⁰⁵ discuss the mechanism of the reactions involved in this hydrolysis, and have obtained results with calcium hydroxide which give promise of commercial possibilities. Working at 350° C. the best yield was 67% of methyl alcohol.

A. Damiens¹⁰⁶ has studied the absorption of ethylene by sulphuric acid in presence of catalysts, the best catalysts being cuprous salts. Under different conditions alcohol, diethyl sulphate, and an oil having the properties of petroleum are formed.

PITCH, ASPHALT, SHALE.

Asphalt.

Air-blown asphalts derived from residual oils have been manufactured for many years, air and steam being blown into the residue at 270°–300° C. for ten to twenty hours. D. Holde and S. Weill¹⁰⁷ have examined such pitches blown at high temperatures and find their saponification values to increase with rise of melting point. The saponification values are much higher than those generally accepted.

Under the action of heat sulphur has the same condensing effect on asphalt as oxygen. Until recently sulphurised asphalts have been completely displaced from the market by blown asphalts owing to the smaller cost of production of the latter, but H. Burnice¹⁰⁸ has reopened the treatment for Roumanian oils, the resulting bitumen being claimed to be of particularly good quality. In treating residues from typical Roumanian crude oils 7·4% of sulphur is required.

¹⁰² *J.*, 1923, 81t.

¹⁰³ *Ber.*, 1922, 55, 3710; *J.*, 1923, 118A.

¹⁰⁴ Cf. *Bur. Mines Tech. Paper* 255.

¹⁰⁵ *Ind. Eng. Chem.*, 1923, 15, 682; *J.*, 1923, 860A.

¹⁰⁶ *Comptes rend.*, 1922, 175, 585.; *J.*, 1922, 957A.

¹⁰⁷ *Petroleum*, 1923, 19, 541; *J.*, 1923, 539A.

¹⁰⁸ *E.P.* 188,354; *J.*, 1923, 46A.

F. Hansgirg and D. Sander¹⁰⁹ give an interesting account of extensive deposits of bituminous marl in Ismid, Asia Minor. The strata are 260 metres thick and there is an estimated quantity of workable marl of 360 million tons, of which the bituminous content, with and without oil, varies from 5 to 20%.

Shale.

J. Takahashi¹¹⁰ has examined the marine kerogen shales of Japan and considers the kerogen to be different from that of ordinary oil-shale. The shales themselves are regarded as dehydrated and partially debituminised sapropelic ooze.

Little advance has been made in the treatment of oil shales, and all attempts to develop an extraction process for removing the oil-producing organic matter have proved unsuccessful. Even on the experimental scale no true solvent has been found capable of extracting the kerogen, though R. H. McKee and R. T. Goodwin¹¹¹ have found that after treatment with such substances as sulphuryl chloride or selenium oxychloride, alcohol will extract as much as 50% of the volatile matter. This effect is probably due to chlorination.

¹⁰⁹ *Petroleum*, 1923, **19**, 576; *J.*, 1923, 757A.

¹¹⁰ *Sci. Rep. Univ. of Japan*, 1922, **1**, 63.

¹¹¹ *Ind. Eng. Chem.*, 1923, **15**, 343; *J.*, 1923, 483A.

COLOURING MATTERS AND DYES.

By JAMES BADDILEY,

British Dyestuffs Corporation, Manchester.

VIEWED from the financial and economic standpoint, the past year can best be described as a lean one for the British dyestuff industry. This was more or less to be expected, of course, with all the conditions operating in an adverse direction, values declining, the textile trade in a state of unprecedented slump, and export business almost entirely excluded on account of the advantages given to the German producers by the exchange factor. It must be said, however, that there were distinct signs of improvement towards the close of 1923. For one thing the recent efforts to stabilise the mark are rapidly lessening the exchange handicap, and, though the position is still confusing, the increase in dyestuff exports, as shown by the Board of Trade returns (19,486 cwt. for December, 1923, as against 7366 cwt. for December, 1922) is a very encouraging sign. The outlook, therefore, has brightened in one direction, but on the whole the conditions prevailing have been a severe test for an infant industry, even with the assistance of such protection as is afforded by the Dyestuffs Act. This very protection, indeed, has its drawbacks for political reasons. No industry comes so much in the limelight as the dyestuff industry, no industry compares with it as "good copy" in the eyes of the Press. Public controversy, as though by magic, increases in acerbity the moment it switches over to the dyestuff question. The result of this state of affairs is that a political bias is given to any discussion of the question which cannot fail to have a deplorable effect. A certain section of opinion exists—though not among the large dyestuff consumers, it should be said—which adopts a more and more prejudiced outlook on this difficult question, and the whole *raison d'être* of the industry which we are slowly and painfully building up seems to be thrust into the background. Even the more logical minds are affected to some extent by contemplation of the possibilities of free trade in dyestuffs, could it be restored. However, the Dyestuffs Act is not the only obstacle to unrestricted traffic in dyestuffs, and the interruption of deliveries of German dyes resulting from various disturbances in Germany's economic life which have occurred recently, has brought home once more the danger of being in a dependent position.

One thing, however, has been noticeable during the past year—namely, that the discontent of the dyestuff consumer has settled down on the one point of price. With regard to the quality of

British-made dyes, and their ever increasing range, there have been general expressions of satisfaction. Mr. Sutcliffe Smith, in his statement to the Annual General Meeting of the Colour Users' Association, on June 19, 1923, stated that there was no reason to doubt the claim of the British makers that they are producing 80% of the colour used in this country. This impression has been generally confirmed by important dye users; that is to say, the position now is just the reverse of the position before the war, when 80% of the country's dyes were imported from abroad. The following estimate for the year 1923, based on the figures available up to the time of writing this report, bears out earlier impressions:—

| | |
|--|-------------|
| Dyestuffs supplied from reparation sources | 1,800 tons. |
| " " " licensed imports | 1,300 tons. |
| | 3,100 tons. |

Estimated total consumption of dyestuffs in the U.K. 13,000 tons.

The whole point of view of the consumers is very plainly stated in the Report of the Colour Users' Association, previously referred to. The other point of view on the price question—that of the dyestuff manufacturers—has been very forcibly expounded by Sir William Alexander in his speech at the Annual Meeting of the British Dyestuffs Corporation (see Press of July 11, 1923). Those interested in this question should read carefully the two speeches referred to.

The general opinion, therefore, is that progress—that is to say, technical progress—is being made. The British dyestuff industry still requires nursing, but is gradually achieving its first object, namely, to render this country substantially independent of foreign dyes. The next object, which is to put the industry in a flourishing condition, depends again on technical progress, not, however, merely in the direction of doing what the Germans had done before, but in the direction of discovery and invention, which will give the industry profit-earning power altogether independent of protective legislation. There is some evidence in the literature review which follows that a start is being made in this direction. In reviewing the published results of technical progress made during the past year one is struck, however, by the fact that the Germans are almost back to their pre-war level as regards output of inventions. There is evidently to be no slackening of effort on their part, and things are not going to be easy for their competitors.

DYESTUFF INTERMEDIATES AND RELATED SUBSTANCES.

Work published during the past year appears to have been mainly along lines established before the war. Azo dyes, vat dyes, and their special intermediates account for the bulk of the

patents. On account of the vast increase in the dyestuff-producing capacity of other countries, it was generally expected that when German colour firms got into stride again after the war, efforts would be made to find fresh fields for development. Some of the lines of manufacture which would naturally link up with experience in the production of dyestuff intermediates had already been adopted, however—photographic and pharmaceutical chemicals, for example.

There are some signs of a new departure on the part of dyestuff firms in the rush of patents for methods of making synthetic resins. Meister, Lucius, u. Brüning has a series of patents for improvements in connexion with the phenol-aldehyde type of resin,¹ in many of which hydroxycarboxylic acids are used instead of the simple phenols. The same firm is working upon a new type of soluble resins obtained by the condensation of amines such as *a*-naphthylamine, xylidine, etc., with formaldehyde or acetaldehyde.² Akt.-Ges. f. Anilinfabr. has also entered this field with a series of patents for the production of resins from tetrahydro-naphthol condensed with formaldehyde or acetaldehyde.³ It is interesting to see in this patent literature how the mind of the dyestuff technologist applies itself to another industry. The general tendency in the synthetic resin industry seems, however, to be in the direction of using less expensive raw materials; for example, in the usual formaldehyde-phenol reaction the formaldehyde is replaced by thionyl chloride,⁴ by sulphur,⁵ or by chlorine.⁶ Going further still in the direction of cheapness, resins have been prepared by the application of polymerising reagents to hydrocarbons, e.g., naphthalene,⁷ or even by the polymerisation of acetaldehyde.⁸

An interesting, though sinister, side-line of the dyestuff industry has been the manufacture of toxic material for warfare. Meister, Lucius, u. Brüning is beating swords into ploughshares in a significant way (this process is always reversible) in a series of patents relating to thiodiglycol, $S(CH_2\cdot CH_2\cdot OH)_2$. This product was, of course, an intermediate stage in the manufacture of "mustard gas" as carried out in Germany. It now appears to find many applications, but it must first be made odourless.⁹ Thiodiglycol

¹ G.P. 364,041-4; G.P. Appl. F.50,661, F.50,965, F.50,976, F.50,977; G.P. 370,605, 365,286, 374,379, 358,401, 357,757, 364,040, 367,758, 362,382; G.P. Appl. F.46,026, F.49,800.

² G.P. Appl. F.47,166; G.P. 305,026, 372,855, 359,676.

³ G.P. 356,223, 356,224, 358,400, 358,399.

⁴ Meister, Lucius, u. Brüning, G.P. 362,383.

⁵ Soc. Chom. Ind. Basle, G.P. Appl. B.98,547.

⁶ Chem. Fabr. Weiler-ter Meer, G.P. 355,173.

⁷ G.P. 380,577; G.P. Appl. F.25,805, C.27,616.

⁸ G.P. Appl. C.29,230, C.31,249; E.P. 187,619.

⁹ G.P. 362,445, 369,424-5.

can then be used for a variety of industrial purposes, e.g., as a solvent for printing colours,¹⁰ and as a softener for synthetic resins.¹¹ Many derivatives of thioglycol, suitable for use as solvents etc., can be prepared by condensing it with aldehydes etc.¹² The formaldehyde condensation product can be used in the preparation of Alizarin lakes.¹³

Fungicides, insecticides, and weed-killers have become another side-line with certain dyestuff manufacturers. The products described in the patent literature are all more or less linked up with dyestuffs intermediates.¹⁴

Some of the ramifications of the industry seem very curious, but the explanation is simple. Speaking generally, the manufacture of dyestuffs themselves has not called forth anything like the same effort as has the technical preparation of the required intermediates. Thus when Perkin discovered mauve in 1856, aniline was a comparatively rare chemical, and as the dyestuff industry developed one of its first problems was the industrial production of aniline oil. As new dyestuffs were discovered the rapid development in the technique of the manufacture of the ever-increasing range of intermediates gave the dyestuff industry a commanding position with regard to aromatic organic products in general and a large portion of the aliphatic field also. Glyoxal is an example of a product for which previously there has not been any industrial demand, but evidence of a new interest in this substance is found in the Weiler-ter Meer patent for its preparation by treating tetrahalogenethane with oleum in the presence of a salt of a heavy metal such as mercury.¹⁵ Production directly from acetylene by the action of a halide salt of a polyvalent metal, preferably gold, is proposed by K. Kindler.¹⁶ Possibilities in connexion with industrial uses of glyoxal are indicated in a patent of Meister, Lucius, u. Brüning, which claims its conversion to tetrahydroxyquinone by the action of alkalis in the presence of air.¹⁷

Sometimes supply comes before demand, especially in the case of organic by-products. Thus we see attempts being made to find outlets for cymene in connexion with dyestuff manufacture. Furfural is another material for which outlets are desired in the organic chemical industry.¹⁸

¹⁰ G.P. Appl. F.49,078.

¹¹ G.P. 370,605.

¹² G.P. 360,980, 365,170, 365,171; U.S.P. 1,422,869.

¹³ G.P. Appl. F.46,592.

¹⁴ G.P. 343,864, 365,169, 376,718; G.P. Appl. F.52,685; G.P. 343,866; G.P. Appl. B.107,638.

¹⁵ G.P. 362,743.

¹⁶ G.P. 362,745.

¹⁷ G.P. 370,222, addition to G.P. 368,741.

¹⁸ *Chem. Trade J.*, 1923, 755.

Two further references will be quoted to show how widespread are the interests of the dyestuff industry. Meister, Lucius, u. Brüning has patented the preparation of organic acids by the action of nitric acid on materials of vegetable origin, such as coal, lignite, etc. The acid products obtained are stated to be capable of finding application, particularly in the paper, leather, and dyeing trades; also in the preparation of colloidal metal solutions for pharmaceutical purposes.¹⁹ The Badische Anilin u. Soda Fabrik has taken out a patent for the preparation of drying oils by the action of phosgene on aliphatic or hydroaromatic hydrocarbons in the presence of aluminium chloride.

A side-line in the dyestuff industry of recent origin is the manufacture of synthetic mordants which take the place of natural tannins in the fixation of basic dyes. These products, which have affinity for cotton, are sulphur condensation products of phenols. Recent developments in connexion with their manufacture are published by F. Bayer u. Co.²⁰ Meister, Lucius, u. Brüning has also entered this field with a patent for the condensation of sulphur chloride with phenols. Products are obtained which possess mordanting properties.²¹

Halogen Compounds.

The most interesting development under this heading is the work by J. Schmidlin (Cassella und Co.) on polychloroaldehydes, which find application in the preparation of triphenylmethane dyes of the Eriochrome Azural type (see later under dyestuffs).

A. Wahl and Soc. Anon. des Matières Colorantes et Prod. Chimiques propose to obtain pure *o*- and *p*-chlorotoluene by sulphonating the mixed chlorination product of toluene. The *o*-chloro compound sulphonates in preference to the *para*, and the latter is thus obtained in a pure state. Pure *o*-chlorotoluene is then recovered from its sulphonic acid by hydrolysis.²²

A new general method of chlorination of organic compounds by means of sulphuryl chloride, in conjunction with aluminium chloride and sulphur chloride, is patented by O. Silberrad and A. Boake, Roberts and Co.²³

Durand et Huguenin has described an interesting new reaction in connexion with the chlorination of primary aromatic amines. If the amine in the form of its hydrochloride is suspended in an indifferent medium and treated with chlorine, very highly chlorin-

¹⁹ G.P. Appl. F.48,809.

²⁰ G.P. Appl. F.50,137, F.50,623, F.49,224.

²¹ G.P. Appl. F.49,214.

²² G.P. Appl. S.53,132.

²³ E.P. 193,200.

ated products are obtained; for example, aniline by this method gives the compounds²⁴ :—



Sulphonation.

By acting on acylamines with chlorosulphonic acid R. N. Johnsen and S. Smiles have obtained sulphonyl chlorides. These substances have the same configuration as those of the sulphonic acids obtained from the acylamine with sulphuric acid.²⁵ In this connexion compare the action of chlorosulphonic acid on aromatic amines, shown by J. Baddiley, J. Payman, and H. Wignall,²⁶ to give *o*-sulphonic acids under certain conditions.

An improvement in the manufacture of aromatic sulphochlorides is claimed by Chem. Fabr. Weiler-ter Meer; instead of the customary excess of chlorsulphonic acid, only one equivalent is used plus an equivalent of SO_3 :— $\text{RH} + \text{ClSO}_3\text{H} + \text{SO}_3 = \text{R-SO}_2\text{Cl} + \text{H}_2\text{SO}_4$.²⁷

Amines.

Much work has been done on the catalytic reduction of nitro compounds (see later under catalysis). Commercial reduction by means of sodium amalgam is proposed by W. G. Adam, N. E. Siderfin, and D. G. Murdoch (Gas Light and Coke Co.), particularly in connexion with the reduction of nitro compounds to hydrazo compounds, *i.e.*, for the synthesis of benzidine etc.²⁸ Provided that there are no technical difficulties, and that the yields are comparable, this process would appear, on the face of it, cheaper than the usual method of using zinc dust. It is not made clear, however, what advantage is achieved by making the sodium amalgam separately in the electrolytic cell and then bringing it into contact with the nitro compound, as against the apparently simpler process of direct electrolytic reduction with the nitro compound itself in the cell.

The direct introduction of amino groups is a problem which has always presented interesting possibilities, economic and otherwise, to the dyestuff technologist. A. E. Tschitschibabin has succeeded

²⁴ E.P. 193,843, 198,676.

²⁵ *Chem. Soc. Trans.*, 1923, **123**, 2384.

²⁶ E.P. 175,019.

²⁷ G.P. 385,049.

²⁸ E.P. 200,167.

in doing this in the case of bases of the pyridine and quinoline series, the reagent used being sodamide. The amino derivatives of these bases might find application in dyestuff synthesis.²⁹

Apart from the references mentioned, recent technical work in connexion with aromatic amines has been mainly in the direction of new syntheses of N-substituted derivatives. Chem. Fabr. Weiler-ter Meer obtains alkylated amines by the reduction of alkylidine compounds with zinc and sulphur dioxide; for example, ethylaniline can be obtained in this way from acetaldehyde and aniline.³⁰ Another method for making monoalkylamines, based on reduction, is that of Chem. Werke Grenzach, in which imino ethers, $R-C(:NH)OEt$, are reduced electrolytically.³¹ Dimethylamines are obtainable, according to Kalle und Co., from phenylimino-diacetic acids, $PhN:(CH_2CO_2H)_2$, or their ring-substituted derivatives by heating them with ferrous salts.³² A new type of substituted amine is suggested by the Akt.-Ges. f. Anilinfabr. patent for the preparation of cyclohexylamines by condensing aromatic primary or secondary amines with cyclohexanol in the presence of zinc chloride.³³

Phenols.

Of the three main technical methods of introducing the hydroxyl group into aromatic compounds, *i.e.*, replacement of the sulpho, halogen, and diazonium groups respectively, there has been no published progress with regard to the first. An interesting observation, however, has been made with regard to the second method by K. W. Rosenmund, K. Luxat, and W. Tiedemann in an investigation on the effect of ultra-violet rays on the reactivity of halogens in the ring of aromatic compounds, both in the presence and absence of catalysts. The effect of ultra-violet rays was found to be very marked; for example, on boiling *p*-chlorobenzoic acid with 35% caustic potash for 6 hours in the presence of copper only 6% of the chlorine was split off, whilst if the reaction was carried out in a quartz vessel exposed to the rays the whole of the chlorine was replaced by hydroxyl.³⁴ An improvement in connexion with the third method of introducing the hydroxyl group (by replacement of the diazonium group) has been patented by H. H. Hodgson and The British Dyestuffs Corporation, Ltd., who find that by continuously steam-distilling off the *m*-chlorophenol from decomposing diazochlorobenzene high yields of the chloro-

²⁹ *Chem. Zentr.*, 1923, **94**, III., 1020, 1026; G.P. Appl. T.19,585.

³⁰ G.P. 367,013.

³¹ G.P. 360,529.

³² G.P. 375,463.

³³ G.P. Appl. A.36,571.

³⁴ *Ber.*, 1923, **56**, 1950.

phenol are obtained.³⁵ *m*-Chlorophenol gives the hitherto unknown nitroso compound when treated with nitrous acid.³⁶

A method for the direct introduction of the hydroxyl group in the case of pyridine, quinoline, and their homologues is described by A. E. Tschitschibabin. These substances are heated with very carefully dried and finely powdered caustic potash. Hydrogen is evolved and the hydroxyl group enters the ring in the α -position to the nitrogen atom.³⁷

According to the Chem. Fabr. auf Actien vorm. E. Schering, improved results are obtained in the manufacture of quinol by reducing quinhydrone by means of a ferrous salt in the presence of an oxide, hydroxide, or carbonate of magnesium, zinc, manganese, or iron. The quinhydrone can be obtained from quinone by the usual reducing agents.³⁸ Quinone itself has usually been prepared by the chromic acid oxidation of aniline. It is now proposed by the Byk Guldenwerke Chem. Fabr. A.-G. to replace a portion of the expensive chromic acid with pyrolusite.³⁹ The electrolytic oxidation of benzene to quinone and the electrolytic reduction of quinone to quinol have been investigated by A. Seyewetz and G. Miodon.⁴⁰

A patent has been taken out by N. E. Siderfin, S. B. Tallantyre, W. V. Shannan, and W. L. Galbraith (Gas Light and Coke Co.) for the preparation of nitrosophenols by the action of nitrosylsulphuric acid on phenols. This method might prove economically advantageous in cases where the nitrosophenol is required for further condensation in sulphuric acid solution, isolation of the nitroso compound being thereby avoided; for example, in the preparation of the indophenol from carbazole and nitrosophenol.⁴¹

Claim is made by the Badische Co. for a process for the preparation of phenol in a form which will not darken. The phenol is boiled for some hours before distillation.⁴²

Aldehydes.

Direct oxidation of dibenzyl to give benzaldehyde and benzoic acid is proposed by H. R. Curme and The Carbide and Carbon Chemical Corporation.⁴³

Of the various derivatives of benzaldehyde the *m*-nitro-compound is one of the most important from an industrial point of view. As

³⁵ E.P. 200,714.

³⁶ E.P. 206,734; *Chem. Soc. Trans.*, 1923, **123**, 2499.

³⁷ *Ber.*, 1923, **56**, 1879.

³⁸ G.P. 380,503.

³⁹ G.P. 369,354.

⁴⁰ *Bull. Soc. Chim.*, 1923, **33**, 449.

⁴¹ E.P. 203,060.

⁴² G.P. Appl. B.103,620.

⁴³ E.P. 197,319.

ordinarily prepared by the direct nitration of benzaldehyde, O. L. Brady and S. Harris show that the maximum yield of pure *m*-compound is 65% of theory, 19% of the *o*-compound being also formed.⁴⁴

A new synthesis of β -resorcylaldehyde by the action of diphenyl-formamidine on resorcinol is described by J. B. Shoesmith and J. Haldane.⁴⁵

Carboxylic Acids.

Improvements in the preparation of benzoic acid are claimed by E. O. Barstow and the Dow Chemical Co., who oxidise benzyl chloride with bleaching powder,⁴⁶ and by R. H. McKee and H. C. Cooper,⁴⁷ who oxidise toluene with chromic acid.

The manufacture of *o*-nitrobenzoic acid by distilling nitrotoluene with strong nitric acid is claimed by E. A. Lloyd, V. P. Gershon, and W. M. Grosvenor.⁴⁸

Kalle u. Co. published an interesting process for the preparation of *o*-aminocarboxylic acids of the benzene series by the action of oxidising agents, especially hydrogen peroxide, on isatin and its derivatives.⁴⁹

Some interesting work has been done recently in connexion with phenylglycine. In the ordinary process of condensing aniline with chloroacetic acid, R. Nodzu and S. Komatzu have shown that in addition to phenylglycine there are formed also phenylimino-diacetic-monoanilide and diphenyldiketopiperazine.⁵⁰ A method for making phenylglycine directly from aniline and trichloroethane, without the intermediate production and isolation of chloroacetic acid, is one that promises to be of great interest from the economical point of view. M. Wyler and The British Dyestuffs Corporation, Ltd., have patented a process for carrying this out in one operation.⁵¹

Derivatives of Naphthalene.

Under this heading come some of the chief dyestuff intermediates which have achieved importance from the point of view of bulk production, yet it is remarkable how little information with regard to them has appeared in the literature in recent years. H. E. Fierz-David reviews the subject generally and gives an indication of the developments of the chemistry of naphthalene in its industrial aspects.⁵²

⁴⁴ *Chem. Soc. Trans.*, 1923, **123**, 484.

⁴⁵ *Ibid.*, 1923, **123**, 2704.

⁴⁶ U.S.P. 1,463,190.

⁴⁷ U.S.P. 1,458,491.

⁴⁸ U.S.P. 1,458,715.

⁴⁹ G.P. 375,616.

⁵⁰ *Chemical Abstracts*, 1923, p. 1449.

⁵¹ E.P. 188,933.

⁵² *Z. angew. Chem.*, 1923, **36**, 188; *J.*, 1923, 421T, 429T.

Interest in the dinitronaphthalenes and nitronaphthylamines has been revived during the year. Of the 10 possible dinitronaphthalenes only four were previously known (1.5, 1.8, 1.3, and 1.6), and of these only the first two, which are direct nitration products of naphthalene, have any industrial application. V. Vesely and K. Dvorak⁵³ have now prepared the 1.7-, 1.4-, and 1.2-dinitronaphthalenes, the first two from the corresponding nitronaphthylamines, the last by dehydrogenation of ar-1.2-dinitrotetrahydronaphthalene (nitration product of tetralin). In the partial reduction of the dinitronaphthalenes it was found that the particular nitro group attacked depends on the reducing agent used (ammonium sulphide or stannous chloride), just as in the analogous case of 1.2.4-dinitrotoluene. In the nitration of acet- β -naphthalide V. Vesely and M. Jakes have observed the formation of 6-nitro-2-acetnaphthalide in addition to the known 1.2- and 8.2-isomers.⁵⁴ A useful summary of the rules of substitution in the naphthalene series is given in tabular form by the same authors.⁵⁵

The interaction of the nitronaphthylamines with formaldehyde has been studied by G. T. Morgan and F. R. Jones.⁵⁶ The resulting products are either methylenebisnitronaphthylamines or diamino-dinitrodinaphthylmethanes, according to the configuration of the particular nitronaphthylamine used. Aeridines were prepared from the methane bases which had two amino groups ortho to the 'methylene bridge.'

A new class of β -naphthol derivatives, the 1-arylamino-2-naphthols, is described by A. Wahl and R. Lantz.⁵⁷ These compounds are prepared by condensing 1-halogen-2-naphthol with aromatic amines. They are converted to the corresponding quinones, e.g., 1-phenylimino-2-naphthoquinone, by oxidation by means of sodium hypochlorite.⁵⁸ The new aryliminonaphthoquinones give typical quinone reactions, e.g., they give sulphonic acids when treated with bisulphite, and add on a molecule of an amine to form 4-arylamino-1-arylimino- β -naphthoquinones.⁵⁹ The latter readily condense with a further mol. of amine to give azines (see later under dyestuffs).

G. T. Morgan and E. Jones⁶⁰ describe the preparation of β -naphthol-4-sulphonic acid by a new method, namely, by heating naphthalene-1-diazo-2-oxide-4-sulphonic acid with alcohol.

⁵³ *Bull. Soc. Chim.*, 1923, **33**, 319.

⁵⁴ *Ibid.*, 1923, **33**, 942.

⁵⁵ *Ibid.*, 1923, **33**, 958.

⁵⁶ *J.*, 1923, 92T.

⁵⁷ Soc. Anon. des Mat. Col. St. Denis, E.P. 182,084; *J.*, 1923, 598A.

⁵⁸ *Rev. Gén. Mat. Col.*, 1923, **28**, 33; E.P. 191,064, 182,084, 206,150.

⁵⁹ E.P. 206,142.

⁶⁰ *J.*, 1923, 97T.

Interesting new sulphur-containing derivatives of naphthylamine- and aminonaphthol-sulphonic acids are described by H. Suida and Chem. Fabr. Weiler-ter Meer. These are prepared by adding sulphur chloride (S_2Cl_2) to aqueous solutions of the sulphonnic acids in the presence of sodium acetate. Unstable compounds are first formed which are very rich in sulphur, and these on treatment with alkali or with strong acids pass, with loss of sulphur, into more stable products. The new compounds easily form deeply coloured oxidation products, which in turn are easily reduced to the leuco state. They appear to retain the diazotising and coupling properties of the original aminonaphthalene- or amino-naphthol-sulphonic acids.⁶¹

Improvements in the manufacture of H-acid are claimed in a patent by G. Pomo and G. Pelligrini.⁶² According to these investigators, it is advantageous to isolate the 1,3,6,8-nitronaphthalenetrisulphonnic acid produced by sulphonation and nitration of naphthalene, and to reduce it by means of hydrogen and a catalyst. More economical working and greater purity of the product are claimed as the result of this invention.

An examination of the constitution and properties of J-acid (2-amino-5-naphthol-7-sulphonic acid) has been made by M. Battegay and A. Wolff in an attempt to arrive at an explanation of the substantive character of the cotton dyes made from this intermediate. Some of the derivatives prepared are new. J-acid itself, also its diazo compound and its hydrazine, were found to have no affinity for cotton. An interesting fact emerged with regard to the hydrazone: those from monoketones have no affinity for cotton, whereas those from α -diketones dye cotton well. The hydrazone from the diketones may be regarded as *o*-hydroxyazo derivatives, from which it may be inferred that the presence of the azo group is an accessory cause at least in connexion with the affinity of J-acid dyes. The "tartrazine" derived from the hydrazone of J-acid (2 mols.) and dioxytartaric acid was also found to dye cotton.⁶³

β -Hydroxynaphthoic acid (2-hydroxynaphthalene-3-carboxylic acid) has attained great industrial importance in recent years on account of the use of its anilide for the production of ice colours on cotton. In view of this it is curious that so many of the isomers of this acid should have remained unknown until the subject was taken up by F. A. Royle, C. Butler, and J. Schedler. These authors have prepared and described the 3-, 4-, 5-, 6-, 7-, and 8-hydroxy- β -naphthoic acids, and also many of their derivatives.⁶⁴ In the

⁶¹ G.P. 380,578.

⁶² E.P. 190,114.

⁶³ Bull. Soc. Chim., 1923, **33**, 1481.

⁶⁴ Chem. Soc. Trans., 1923, **123**, 1641, 1649.

preparation of β -hydroxynaphthoic acid itself E. C. Shorey claims to obtain improved yields by continuously circulating the gas during the interaction of carbon dioxide and sodium naphtholate. Free β -naphthol is removed from the sphere of reaction by this means.⁶⁵

The arylamides of β -hydroxynaphthoic acid have not previously been sulphonated. Meister, Lucius, u. Brüning now describes sulphonic acids obtained by treatment of the arylamides with monohydrate. No definite constitution is attributed to them, but they are described as giving aqueous solutions which have marked colloidal properties.⁶⁶

Various new arylides of β -hydroxynaphthoic acid have come into prominence during the year, but these will be referred to under the heading of azo dyes. The colloidal character of these arylides is of great importance in connexion with their application to the cotton fibre. Under the ultra-microscope and in ultra-filtration they show typical colloidal behaviour. Solutions of β -naphthol do not possess these properties under analogous conditions, and this difference will account for the great advantages of the Naphthol AS series over β -naphthol with regard to ease of application in dyeing processes, i.e., Naphthol AS is applied to the fibre by padding and squeezing, and is developed directly without drying, whereas the β -naphthol preparation requires to be dried before it can be developed.⁶⁷

Miscellaneous Intermediates.

Some additions have been made to our information with regard to the chemistry of acenaphthene during the past year. The bromine derivatives have been studied by R. de Fazi.⁶⁸ In the nitration of 3-chloro-acenaphthene G. Farnell finds that the 3-chloro-4-nitro-derivative is formed together with another product.⁶⁹ It is only during comparatively recent times that acenaphthene has been isolated from coal tar on the industrial scale, but there are indications that its chemistry will eventually be thrashed out as thoroughly as was the chemistry of naphthalene in the earlier days of the dyestuff industry. The same may be said of carbazole, but at present technical progress has been mainly on the lines of the isolation and purification of this substance⁷⁰ and in connexion with the preparation of its alkyl derivatives.

A simple method of making the latter is described by T. S. Stevens and S. H. Tucker.⁷¹ The carbazole is dissolved in alcohol or acetone, to which is added an aqueous solution of sodium or

⁶⁵ U.S.P. 1,450,990.

⁶⁶ E.P. 183,428.

⁶⁷ J. Soc. Dyers & Col., 1923, **39**, 334.

⁶⁸ Gazz. Chim. Ital., 1923, **53**, 499.

⁶⁹ Chem. Soc. Trans., 1923, **123**, 60.

⁷⁰ G.P. Appl. W.62,045.

⁷¹ Chem. Soc. Trans., 1923, **123**, 2140.

potassium hydroxide, followed by the alkylating agent, e.g., methyl sulphate. The reaction proceeds at, or slightly above, room temperature, and the yield is stated to be practically quantitative.⁷²

A new derivative, namely, *p*-nitrophenylcarbazole, is prepared by G. and M. de Montmollin⁷³ by the action of nitrobenzene on the sodium or potassium derivative of carbazole. Many derivatives of tetrahydrocarbazole are described by G. A. Edwards and S. G. P. Plant.⁷⁴

A patent for the preparation of aminophenanthrenequinones, by reducing the corresponding nitro compounds with hydro-sulphite, is suggestive of new developments.⁷⁵

Catalysis.

• A remarkable number of patents dealing with catalysis have been published by German colour firms during the past year or so. These firms seem to have been engaged largely in developing the manufacture of highly active charcoal from such raw materials as lignite. A very large number of patents have been published in connexion with the manufacture and use of specially active charcoal, but so far only one or two have had a direct bearing on the dyestuff industry. For example, F. Bayer u. Co. patents the production of aromatic amines by reducing the corresponding nitro compound by means of coke-oven or producer gas, containing hydrogen sulphide, in the presence of porous charcoal.⁷⁶ The capacity of some of the charcoals described for the absorption of vapours is remarkably high, even under diminished pressure; for example, F. Bayer u. Co. describes the use of absorbent charcoal for protecting the vacuum pump against the action of corrosive vapours during the distillation of *p*-nitrobenzoyl chloride.⁷⁷

Methyl alcohol and formaldehyde are important raw materials of the dyestuff industry. Various factors—for example, the synthetic manufacture of acetic acid—have had a disturbing effect on the wood distilling industry, with the result that the price of methyl alcohol, and consequently of formaldehyde, shows a strong upward tendency. In consequence of this the synthetic production of both of these materials has attracted a considerable amount of attention. Recent publications refer to the catalytic production of formaldehyde from methane, from methylene chloride, and from carbon dioxide, and of methyl alcohol from methyl chloride.⁷⁸

⁷² Cf. also E.P. 192,376; National Aniline & Chemical Co.

⁷³ *Helv. Chim. Acta*, 1923, **6**, 94.

⁷⁴ *Chem. Soc. Trans.*, 1923, **123**, 2393.

⁷⁵ G.P. 873,976.

⁷⁶ G.P. Appl. F.49,396.

⁷⁷ G.P. Appl. F.49,623.

⁷⁸ *Z. angew. Chem.*, 1923, **36**, 297; *Chem. Zentr.*, 1923, **94**, III., 610; G.P. 362,746, 361,042; U.S.P. 1,460,244.

The catalytic reduction of nitro compounds has been under discussion for some years, but a considerable volume of literature on this subject is still being published, particularly a series of papers by O. W. Brown and C. O. Henke, who also have filed patents which embody their discoveries. They use a wide range of catalysts, including thallium, lead, bismuth, tin, oxide of tin, amorphous red lead, etc. In the reduction of nitrobenzene the process can be carried to the azoxy, azo, hydrazo or amino stages, according to the conditions and the catalyst used.⁷⁹

A. Blochet has published an account of the reduction of nitro-compounds using a nickel catalyst.⁸⁰ He shows that reduction can be carried out at moderate temperatures and pressures, e.g., nitrobenzenes may be reduced in the liquid phase; solvents may be employed in the case of a solid nitro compound.

The preparation of β -naphthylamine by the action of ammonia on β -naphthol in the vapour phase in the presence of a catalyst has been proposed by A. Lowy and A. M. Howard.⁸¹

One of the most important and recent developments in connexion with catalysis, so far as the organic chemical industry is concerned, is catalytic oxidation. The success of the phthalic anhydride process worked out in America is now well-known. A. Wohl, who took out patents for this process in Germany⁸² at or about the same time as H. D. Gibbs in America, has now followed with a process for the production of acids, ketones, and carbonyl compounds generally, using metallic salts of oxygen-carrying acids, e.g., sodium vanadate. The manufacture of anthraquinone from anthracene would appear to be one of the main objects of these patents.⁸³ H. D. Gibbs is also working in the field and claims to obtain both anthraquinone and phthalic anhydride by the catalytic oxidation of crude anthracene, the phthalic anhydride being derived from the phenanthrene present.⁸⁴ The Barrett Co. is interested in the catalytic oxidation of acenaphthene to acenaphthenequinone and naphthalic anhydride,⁸⁵ also in the oxidation of aliphatic side chains to aldehydes,⁸⁶ and in the oxidation of benzene to give maleic acid.⁸⁷

A catalytic oxidation of quite a different character from those enumerated above, and interesting for its novelty as an industrial

⁷⁹ U.S.P. 1,451,489, 1,456,969.

⁸⁰ *Bull. Soc. Ind. Mulhouse*, 1922, **88**, 703.

⁸¹ U.S.P. 1,449,423; *Ind. Eng. Chem.*, 1923, **15**, 397.

⁸² G.P. 379,822.

⁸³ G.P. 349,089.

⁸⁴ U.S.P. 1,444,068.

⁸⁵ U.S.P. 1,439,500.

⁸⁶ E.P. 189,107.

⁸⁷ G.P. 365,894.

proposal, is that by A. Eckert. He finds that anthraquinone catalyses the spontaneous oxidation in sunlight of toluene and its homologues to carboxylic acids. The chief drawback of this process would be the time of operation, six weeks' exposure, for example, being necessary in order to obtain a 40% yield of benzoic acid from toluene.⁸⁸

In the preparation of tetrahydronaphthalene by hydrogenation of liquid naphthalene under pressure a mixed nickel-copper catalyst is claimed by the Akt.-Ges. f. Anilinfabr. to be advantageous.⁸⁹ The Badische Co had previously patented the use of boron and chromium compounds along with nickel catalysts for the hydrogenation and dehydrogenation of carbon compounds.⁹⁰

AZO DYES.

In addition to the technical progress revealed in the numerous azo dye patents, the chemistry of the azo and diazo compounds has received a certain amount of attention during the past year. G. T. Morgan and G. R. Davies have published a paper on the upper limits of diazotisability in the benzene series. In the case of triaminomesitylene they found that only two of the amino groups could be diazotised.⁹¹ G. T. Morgan and H. N. Read have studied the diazo reaction in the carbazole series and have described carbazole-3-diazoimine and 3-diazonium salts.⁹²

Witt's method of diazotisation in concentrated nitric acid has been studied by L. Elion, who finds that certain groups (COOH, COCH₃ and CHO) are sometimes displaced by NO₂.⁹³ From further (contradictory) contributions on this subject by L. Elion and by W. Fuchs it appears that the concentration of the nitric acid employed is of vital importance.⁹⁴

Azo derivatives of indoxylo have been investigated by O. Dornier and J. Martinet,⁹⁵ and azo dyes from N-alkyl- α -methylene-dihydro-quinolines are described by W. König.⁹⁶ These compounds have only academic interest.

F. D. Chattaway and H. R. Hill draw attention to the formation of *ortho*- as well as of *para*-hydroxyazo-compounds during the coupling of phenols.⁹⁷

⁸⁸ E.P. 182,487.

⁸⁹ G.P. 369,944.

⁹⁰ G.P. 362,143.

⁹¹ *Chem. Soc. Trans.*, 1923, **123**, 228.

⁹² *Ibid.*, 1922, **121**, 2709.

⁹³ *Rec. Trav. Chim.*, 1923, **42**, 145.

⁹⁴ *Ibid.*, 1923, **42**, 511, 513.

⁹⁵ *Rev. Gén. Mat. Col.*, 1923, **28**, 65, 85.

⁹⁶ *Ber.*, 1923, **56**, 1543.

⁹⁷ *Chem. Soc. Trans.*, 1922, **121**, 2756.

C. W. Porter and K. H. Ihrig make the interesting observation that an asymmetric dye from *m*-aminomandelic acid and β -naphthol can be resolved. Wool takes up the dextro form faster than the laeve form, indicating a chemical union in the dyeing process.⁹⁸

The bisulphite compounds of azo dyes have been further studied by N. N. Woroshzow.⁹⁹ This subject has recently acquired a new interest from the proposal of the Badische Company to use the bisulphite compounds of otherwise insoluble azo dyes in connexion with the dyeing of acetylcellulose.¹⁰⁰

Perhaps the outstanding feature of the year's publications concerning azo dyes is the influx of patents relating to the colours obtained from the arylides of β -hydroxynaphthoic acid. Although the discovery of the Chem. Fabr. Griesheim-Elektron is now ten years old, the original anilide of β -hydroxynaphthoic acid (Naphthol AS) has practically had the field to itself. The red produced when cotton is prepared with Naphthol AS and developed with diazotised *m*-nitro-*p*-toluidine has established itself among the fastest of cotton dyes; for example, in the important trade of bleaching goods containing coloured effects, this red is on a par with some of the best of the vat dyes. It is not surprising, therefore, that efforts should be made to widen the range of shades, especially in the direction of a black. The blue obtained from Naphthol AS and tetrazotised dianisidine had already had a certain measure of success, but the great desideratum is a black having as good properties as the original red.

Patents claiming to produce blacks and other deep shades which are fast to chlorine have been taken out by the Chem. Fabr. Griesheim-Elektron. Cotton is prepared with an arylide of β -hydroxynaphthoic acid, e.g., the anilide, α - or β -naphthalide, etc., and developed with a diazotised aminazo base of the type aryl-azo-*a*-naphthylamine. In the preparation of the base any arylamine may be coupled with any derivative of *a*-naphthylamine capable of coupling in the 4-position. Sulphonic acid groups are ruled out for obvious reasons.¹⁰¹ Another method for obtaining blacks and dark-violet shades is to develop with tetrazotised diaminoazo compounds, e.g., *p*-aminobenzene-azo-cresidine, *p*-aminobenzene-azo-*a*-naphthylamine, etc.¹⁰² F. Bayer und Co. has also entered this field with a claim to obtain fast blacks by the use of a developer of the amino-azo type, prepared from a negatively substituted *o*-amino-

⁹⁸ J. Amer. Chem. Soc., 1923, **45**, 1990.

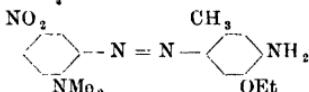
⁹⁹ Chem. Zentr., 1923, **94**, III, 615.

¹⁰⁰ E.P. 204,280.

¹⁰¹ E.P. 203,032; G.P. Appl. C.30,757, C.32,107.

¹⁰² G.P. Appl. C.32,160.

dialkylaniline by diazotising and combining with an amine of the *para* coupling type. For example, the base,



develops a black on Naphthol AS which is stated to be fast to boiling, chlorine, and light.¹⁰³

Many variations of the simple arylides of β -hydroxynaphthoic acid appear in the recent patents of the Chem. Fabr. Griesheim-Elektron. A special claim is made for the *o*-toluidide of β -hydroxynaphthoic acid, especially when halogen-substituted. Unexpected fastness is claimed particularly when the diazo compound used for development is also halogen-substituted.¹⁰⁴ Other patents cover the *o*-alkyloxyarylides¹⁰⁵ and the *p*-alkyloxyarylides. The latter would appear to be specially valuable when used in conjunction with the diazo compound from 5-nitro-*o*-toluidine, bright, fast pinks being claimed.¹⁰⁶ Meister, Lucius, u. Brüning has entered this section of the field with a patent covering *o*-alkoxy-, *o*-aryloxy-, and *o*-aralkyloxy-arylides of β -hydroxynaphthoic acid,¹⁰⁷ and with another patent covering halogenated *p*-alkyl- or *p*-alkoxy-arylides of β -hydroxynaphthoic acid.¹⁰⁸ These naphthols are applicable with any base and are stated to be fast to *kier-boiling*. The Soc. Chem. Ind. in Basle also contributes a patent which relates to the use, in conjunction with any arylide of β -hydroxynaphthoic acid, of the particular bases containing an *o*-alkoxy or aralkoxy group, e.g., 2-amino-4-chlorobenzene-1,1'-phenyl ether.¹⁰⁹

The patents references recorded above appear to indicate a tendency to overlapping between the Chem. Fabr. Griesheim-Elektron and its competitors with regard to the minutiae of the β -hydroxynaphthoic-arylide colours. It is noteworthy, however, that the Griesheim-Elektron is once more the pioneer in what might prove to be quite an important enlargement of the new field of ice colours opened up by the introduction of Naphthol AS. A yellow to go along with this range is suggested by recent patents covering insoluble dyes, formed in substance or on the fibre, which are obtained by coupling a diazo compound devoid of sulpho or carboxy groups with a di-acetylactoarylide of the general formula $\text{Ac}.\text{CH}_2.\text{CO.NH. X.NH.CO.CH}_2.\text{Ac}$, where X is a diphenyl residue.

¹⁰³ E.P. 204,514; G.P. 381,916, 382,087.

¹⁰⁴ E.P. 199,771.

¹⁰⁵ U.S.P. 1,457,114; G.P. Appl. C.31,680.

¹⁰⁶ G.P. 385,955; E.P. 200,739.

¹⁰⁷ E.P. 193,834.

¹⁰⁸ E.P. 193,866.

¹⁰⁹ E.P. 202,984.

For example, di-acetoacetbenzidinide, $\text{CH}_3\text{CO.CH}_2\text{CO.NH.C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH.CO.CH}_2\text{CO.CH}_3$, and di-benzoylacetbenzidinide, $\text{C}_6\text{H}_5\text{CO.CH}_2\text{CO.NH.C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH.CO.CH}_2\text{CO.C}_6\text{H}_5$, are stated to give fast yellows with the diazo compounds from *o*-chloroaniline etc.¹¹⁰

Many new "Naphthols" and new bases have been recently put on the market by the Griesheim-Elektron.¹¹¹ A number of new members of the Rapid Fast series (mixture of stable isodiazotates with β -hydroxynaphthoic arylides) have also been put out. These latter are particularly applicable in calico printing.¹¹²

In connexion with mordant azo dyes, one of the most interesting developments during the last few years has been the preparation of their soluble copper and chromium compounds. The soluble copper compounds of certain types of mordant azo dyes for wool have long been known, but in recent years the Society of Chemical Industry in Basle has patented the preparation of a number of different types of direct cotton colours containing copper. The last patent on this subject describes the copper compounds of azo dyes derived from 2-amino-1-hydroxybenzene-4-sulphonamide (2 mols.) combined with 5,5'-dihydroxy-2,2'-dinaphthylamine-7,7'-disulphonic acid. The products dye cotton in violet shades distinguished by great fastness to light.¹¹³ The same firm has been engaged in the preparation of soluble chromium compounds of mordant-azo wool dyes; various methods of bringing about their formation are resorted to, e.g., treating the sodium salt of the dye with an alkaline chromite or carrying out the azo coupling itself in the presence of an alkaline chromite, etc.¹¹⁴

The Akt.-Ges. f. Anilinfabr. has a series of patents for mordant azo dyes from polychloro-*o*-aminophenols combined with naphthol sulphonic acids. Amongst the diazo components mentioned are 3,4,6-trichloro-2-amino-1-hydroxybenzene, 3,4,5-trichloro-2-amino-1-hydroxybenzene, 3,4,5,6-tetrachloro-2-amino-1-hydroxybenzene, 3,5-dichloro-4-methyl-2-amino-1-hydroxybenzene, and 3,5,6-trichloro-4-methyl-2-amino-1-hydroxybenzene.¹¹⁵ These new dyes give blue shades by the metachrome process.

Chrome printing colours derived from resorcylic acid have been obtained by the Soc. Chem. Ind. in Basle by coupling with 1.diazo-2-naphthol-4-sulphonic acid or its nitro derivative. The shades obtained are violet and violet-brown.¹¹⁶

A new chrome printing dye giving greenish-yellow shades is

¹¹⁰ G.P. Appl. C.31,468, C.32,616.

¹¹¹ J. Soc. Dyers & Col., 1923, **39**, 334.

¹¹² G.P. Appl. C.31,916.

¹¹³ G.P. 369,584.

¹¹⁴ E.P. 191,972; G.P. 369,585.

¹¹⁵ G.P. 364,829, 367,362, 368,958, 368,959; E.P. 192,438.

¹¹⁶ G.P. 367,716, 379,614; U.S.P. 1,437,758.

described by F. Bayer u. Co. It is obtained by coupling diazotised *p*-phenylenediamine-2,6-disulphonic acid with salicylic or cresotinic acid.¹¹⁷

Another chrome printing colour is obtained by the Soe^r Chem. Ind. in Basle by coupling arylpyrazolones derived from *m*-amino-benzoic acid with diazotised 6-amino-4-sulphosalicylic acid.¹¹⁸

A chrome dye giving on wool a black fast to potting is obtained by the same firm from 4- (or 6-)nitro-2-aminophenol diazotised and coupled with 1,5,7-aminonaphtholsulphonic acid.¹¹⁹

A new series of direct cotton dyes, particularly adapted for after-treatment on the fibre with copper or other metallic salts, is described by F. Bayer und Co. The dicarboxylic acid of benzidine (4,4'-diaminodiphenyl-3,3'-dicarboxylic acid) is diazotised and coupled with 1 mol. each of two different end components, one of which contains solubilising sulphonic acid or carboxylic acid groups. When dyed on cotton a wide range of shades is obtained, generally changing on coppering to deeper shades which are fast to light and washing. For example, benzidinedicarboxylic acid combines with 1 mol. of phenyl-β-naphthylamine and 1 mol. of 5,5'-dihydroxy-2,2'-dimaphthylamine-7,7'-disulphonic acid to give a violet changing to blue on after-treatment with copper.¹²⁰

Another new type of direct cotton dye is described in the patent of J. Baddiley, J. Payman, E. G. Bainbridge, and the British Dyestuffs Corporation, Ltd. These dyes contain the pyrazolone nucleus, but substantive properties are derived from the presence of arylbenzothiazole residues. As an example the hydrazine derived from dehydrothiotoluidinesulphonic acid is condensed with dioxytartaric acid after the manner of the analogous synthesis of Tartrazine. The new products dye cotton generally in orange shades fast to light and washing.^{120A}

Apart from the above novelties, the direct cotton colour patents recently published follow along the established lines, except that the benzidine type is not represented. The "straight-chain" type is represented by simple secondary disazo dyes in a patent of F. Bayer und Co., of which the following is an example:—5-amino-2-acetylaminino-1-anisol + 1-amino-2-methoxynaphthalene-6-sulphonic acid + 1,4-naphtholsulphonic acid. The acetyl group is finally split off and the product is a developing blue giving shades fast to washing and light, and dischargeable with hydrosulphite.¹²¹ An extreme degree of complexity in the "straight-chain" type is shown in the Akt.-Ges. f. Anilinfabr. patent for tetrakisazo dyes having the general

¹¹⁷ G.P. 367,862.

¹¹⁸ G.P. Appl. G.52,684.

¹¹⁹ G.P. Appl. G.55,931; E.P. 193,385.

¹²⁰ G.P. 380,058, 382,427; E.P. 198,634, 198,398.

^{120A} E.P. 185,880.

¹²¹ E.P. 201,150.

structure $R\cdot N_2\cdot R^I\cdot N_2\cdot R^{II}\cdot N_2\cdot R^{III}\cdot N_2$ + a nitro-*m*-phenylenediamine. The usual first and middle components may be used; for example, the dyestuff built up from 2,4,8-naphthylaminedisulphonic acid + *o*-naphthylamine + *m*-toluidine + *m*-toluidine + nitro-*m*-phenylenediamine is a direct reddish-brown. Other components give various shades of brown, claimed to be very fast to light.¹²²

Direct dyes of the J-acid group are only represented by one patent (by F. Bayer u. Co.). *p*-Amino-aroyleaminosalicylic acid is diazotised and combined with a heteronuclear amino derivative of J-acid, re-diazotised and coupled with an *a*-naphtholsulphonic acid. For example, the components *p*-aminobenzoyl-*p*-aminosalicylic acid + *m*-aminophenyl-1,2-naphthiminazole-5-hydroxy-7-sulphuric acid + 1,4-naphtholsulphonic acid give a direct red, fast to light, acids, and water.¹²³

The "phosgene" or "urea" type of direct cotton colour is represented by one patent, again by F. Bayer u. Co. An aminobenzoyl derivative of a monoacidyl diamine is diazotised and coupled with an aminoarylpyrazolone. The resulting aminazo compound is treated with phosgene to form the urea, then the acetyl group is removed by hydrolysis. The products are developing yellows of pronounced green tone and having a good fastness to washing and light.¹²⁴

Another developing pyrazolone dye of F. Bayer u. Co. is made from the same end components as the above (an aminoarylpyrazolone) but in simple disazo combination with a tetrazotised aminobenzoyl-diamine; e.g., *p*-aminobenzoyl-*m*-phenylenediaminesulphonic acid is tetrazotised and coupled with 2 mols. of *m*-amino-phenylmethylpyrazolone. A dye similar to the developing yellow mentioned above is claimed.¹²⁵

Wool dyes of the pyrazolone series are represented by two patents. In the first the Soc. Chem. Ind. in Basle claim level-dyeing, light-fast yellows obtained by coupling diazo compounds with 1-(2'-methyl-3'-sulpho-5'-isopropyl)-phenyl-3-methyl-5-pyrazolone.¹²⁶ In the other patent Meister, Lucius, u. Brüning claims that by coupling the diazo compound of *m*-aminobenzaldehyde (or a derivative) with a pyrazolone, dyestuffs are obtained which exceed in fastness properties the hitherto known yellow level-dyeing dyestuffs of the pyrazolone series.¹²⁷

Diphenyline has not hitherto been used as an azo dye intermediate, but now F. Bayer u. Co. claims trisazo dyes made from it by tetrazotising and coupling with 1 mol. of H-acid in acid solution.

¹²² G.P. Appl. A.36,189.

¹²³ G.P. 366,530.

¹²⁴ G.P. 374,991.

¹²⁵ G.P. Appl. F.50,174.

¹²⁶ U.S.P. 1,447,485; G.P. Appl. G.56,117.

¹²⁷ E.P. 205,503.

A diazotised monoamine is coupled on the other side of the H-acid in alkaline solution and the free diazo group of the dephenyline is coupled with a diamine or a phenol. New black dyes are obtained which, unlike the corresponding dyes derived from benzidine, have no affinity for cotton but function as acid dyes and are particularly useful for leather dyeing. The patentees claim that the diphenyline need not be isolated from the benzidine mother liquors in which it occurs but that this liquor may be used directly.¹²⁸

Acid wool dyes which combine level dyeing properties with good fastness to light and tolerable fastness to milling can be made from γ -acid and its derivatives by coupling in the 1-position. The Soc. Chem. Ind. in Basle and H. Schweitzer claim an advance on previously known dyes of the series by the use of a diazo compound obtained from a 4-nitroaniline-2-sulphonamide, e.g., 4-nitroaniline-2-sulpho-ethylanilide (NO_2) (NH_2) $\cdot \text{C}_6\text{H}_3\text{SO}_2\text{N}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)$. Navy blue shades are obtained.¹²⁹ The γ -acid may be replaced by 2,8-naphthylaminesulphonic acid and its derivatives with a similar result except that the shades obtained are redder.¹³⁰

The violet monoazo dye obtained by coupling diazotised *p*-nitroaniline-*o*-sulphonic acid with γ -acid in acid solution is, according to D. E. McAllister and E. J. du Pont de Nemours Co., capable of giving lakes when precipitated by means of a barium salt on an aluminium hydroxide substratum.¹³¹

Another lake dye claimed by F. Bayer u. Co. to give a yellowish-red distinguished by covering power and fastness to light, is obtained by diazotising *m*-toluidinesulphonic acid and coupling with β -naphthol.¹³²

Dyestuffs insoluble in water and oil are obtained according to O. Matter by combining various diazotised amines with 4-nitro-1-naphthol. They can be used as pigments or can be produced on cotton by the Para Red method.¹³³ A general claim is also made for azo dyes from other nitronaphthols, such dyes being produced on the fibre, or in bulk.¹³⁴

TRIPHENYLMETHANE DYES.

This group of dyes was one of the earliest to be discovered, and after a period of intensive development progress in it appeared to cease for a while. A revival took place when the mordant dyes of this group, containing salicylic or cresotinic acid, began to attract attention and the flow of patents began once more. These mordant

¹²⁸ G.P. Appl. F.48,683.

¹²⁹ U.S.P. 1,429,781.

¹³⁰ U.S.P. 1,429,782.

¹³¹ U.S.P. 1,434,619.

¹³² G.P. 366,168.

¹³³ G.P. Appl. M.65,584, M.65,667.

¹³⁴ G.P. Appl. M.67,824.

triphenylmethane dyes are generally characterised by great brilliance of tone, and by giving violet to greenish-blue shades. It is their brightness which has given them utility, for they contrast strongly in this respect with the comparatively dull azo-mordant colours. Unfortunately, they have the drawback of looseness to light, which is, broadly speaking, a defect of the whole group of triphenylmethane dyes. J. Schmidlin and Cassella u. Co., in a series of patents, the first of which appeared about the beginning of the war, claim to have made an important advance with regard to light-fastness in mordant dyes derived from an aromatic aldehyde condensed with two mols. of salicylic or cresotinic acid, the novelty consisting in the use of a highly chlorinated aldehyde, e.g., tetrachlorobenzaldehyde.¹³⁵ Outstanding milling fastness and purity of tone are claimed for the dyes made from 2,4,5-trichlorobenzaldehyde.¹³⁶ The chloro-aldehydes are obtained by chlorinating toluene, using an iron catalyst, fractionating until the required chlorotoluene is sufficiently pure, then chlorinating the side chain in ultra-violet light. The resulting polychlorobenzal chloride can be converted into aldehyde with sulphuric acid or can be condensed directly with cresotinic acid. Analogous dyes have been obtained from halogenated xylenes.¹³⁷

A modification of the aurine-tricarboxylic acid type of mordant triphenylmethane dyes is introduced by the firm of Durand et Huguenin. In this case the dianilide of a methylene-di-*o*-hydroxy-carboxylic acid is condensed with salicylic or cresotinic acid. The anilido groups permit the introduction of sulphonate acid groups, in which case dyes are obtained of particular value for chrome-printing purposes, being more vivid, intense, and fast than the old Chrome Violet.¹³⁸ In a later patent the simple diamide of methylene-disalicylic acid is condensed with salicylic or cresotinic acid. Sulphonation is not necessary in this case in order to obtain useful dyes. Greater fastness is claimed than in the case of sulphonated amides.¹³⁹

A new departure in the shape of trinaphthylmethane dyes which are analogous to the aurines has been made by the Soc. Chem. Ind. in Basle. These dyes are formed by the action of carbon tetrachloride on *o*-naphthol or 1-naphthol-2-carboxylic acid in the presence of caustic alkali.¹⁴⁰ Subsequent patents help to clear up the course of the reaction, for it is found that when carbon tetrachloride reacts on 1-naphthol-2-carboxylic acid, in addition to the

¹³⁵ U.S.P. 1,428,984.

¹³⁶ G.P. 363,290.

¹³⁷ G.P. 344,900, 360,414, 364,730.

¹³⁸ E.P. 166,530.

¹³⁹ E.P. 183,123.

¹⁴⁰ E.P. 172,177.

lyestuff, there are also formed 4,4'-dihydroxy-3,3'-dicarboxy-1,1'-dinaphthyl ketone and 1-naphthol-2,4-dicarboxylic acid.¹⁴¹ Aliphatic alcohols have a powerful influence on this reaction. If alcohol is present when carbon tetrachloride acts on *a*-naphthol here are formed esters of 1-naphthol-4-carboxylic acid, and 1-naphthol-2,4-dicarboxylic acid, as well as 4,4'-dihydroxy-1,1'-dinaphthyl ketone.¹⁴² A further development of the invention refers to trinaphthyl- or dinaphthylphenyl-methane dyes obtained by reacting with a phenyl- or naphthyl-chloroform on an *a*-naphthol derivative having a free 4-position. The dyes from 1-naphthol-2-carboxylic acid (*e.g.*, by reacting with benzotrichloride) are particularly interesting, being chrome-greens fast to milling and potting.¹⁴³ In this reaction also the intermediates first formed can be isolated; thus benzotrichloride forms with 1-naphthol-2-carboxylic acid the 1-phenyl-ketone-4-hydroxynaphthalene-3-carboxylic acid.¹⁴⁴ The latter can be decarboxylated by heating with diluent to give 4-hydroxynaphthalene-1-phenyl ketone. Similarly the previously mentioned dihydroxydicarboxydimaphthyl ketone gives 4,4'-dihydroxy-1,1'-dinaphthyl ketone.¹⁴⁵

The well-known "ketone" synthesis of triphenylmethane dyes, hitherto generally limited to the ketones from tertiary bases, has been extended by J. Baddiley and E. H. Rodd (British Dyestuffs Corporation, Ltd.) to ketones derived from monoalkyl-*o*-toluidines. Thus the ketone derived from monoethyl-*o*-toluidine by condensing it with formaldehyde, sulphurising the "methane base" thus formed, and finally hydrolysing the thioketone, is condensed with secondary and tertiary amines to give a series of bright basic dyes from which, in certain cases (*e.g.*, when benzyl residues are present), acid dyes can be prepared by sulphonation. These latter are generally level-dyeing wool violets, tending to the red side.¹⁴⁶

INDIGOID DYES.

In connexion with indigo itself, the most noteworthy publication of the year is that of a new indigo-dyeing process and of new products for this purpose. As the chemistry of indigo was gradually unfolded after the first synthesis, attempts were made to improve the cumbersome vat-dyeing process. A. v. Baeyer's original synthesis was made use of by the Badische Co., who put *o*-nitrophenylpropionic acid on the market for use in printing. Another product was Kalle's Indigo Salt I, *o*-nitrophenyllactic acid methyl ketone, also used for printing. A further attempt

¹⁴¹ E.P. 195,513.

¹⁴² E.P. 181,009.

¹⁴³ U.S.P. 1,460,315.

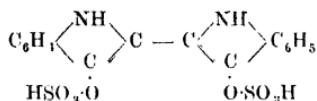
¹⁴⁴ G.P. 378,908; E.P. 203,824.

¹⁴⁵ G.P. 378,909.

¹⁴⁶ E.P. 189,295.

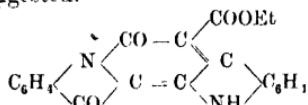
was made by the Badische Co. in their Indophor process, which made use of indoxylcarboxylic acid, this being printed and then converted into indigotin by passage through an acidified solution of ferric chloride.

All these processes, and many others that were proposed, failed for one reason or another, but generally on account of the low yield of indigotin eventually obtained as a result of performing what practically amounted to a synthesis on the fibre. The firm of Durand et Huguenin now claims to have found a solution of the problem in the use of enolic esters of leuco-indigotin which are formed by the reaction of acids with the -OH group of the leuco-indigotin, for instance, the compound



which is obtained by the action of sulphonating agents, e.g., chlorosulphonic acid, sodium chlorosulphonate, or oleum, on leuco-indigotin in the presence of a tertiary base such as pyridine. The new esters are used in the form of neutral salts, e.g., sodium salts, in which form they are easily soluble, stable against oxidation, and can be applied to textiles by either dyeing or printing methods. After impregnation the dye is developed by hydrolysis or by oxidation, for example, by passage through ferric chloride or bichromate baths. It is claimed that the conversion to indigotin is almost quantitative. The new process looks very attractive from the point of view of the calico printer or of the wool dyer who is not equipped with special indigo-vat plant. The invention is stated to be applicable to other vat dyestuffs besides indigotin.¹⁴⁷

T. Posner and G. Pyl describe a new violet-red vat dye obtained by the action of malonic ester on indigotin, for which the following constitution is suggested.¹⁴⁸



By treating *o*-tolylindigotin with nitrous gases in the presence of ether, T. Posner and W. Heumann have obtained dinitrosodi-hydroxydihydrotolylindigotin. *m*-Toluoylformic ester is produced if the reaction is carried out in alcohol instead of ether.¹⁴⁹

K. Kunz has described complex copper, zinc, and nickel compounds of indigotin which contain two molecules of indigotin in combination with one atom of metal. These are formed by heating

¹⁴⁷ E.P. 186,057, 202,630, 202,632, 203,681.

¹⁴⁸ Ber., 1923, 56, 31.

¹⁴⁹ Ber., 1923, 56, 1621.

indigotin with the metal powder in an indifferent solvent. The substances are highly unstable towards acids, but very resistant to alkalis. Complex compounds are also formed with alkali metals, which are extremely easily converted back to indigotin by water. Thioindigo also undergoes this reaction.¹⁵⁰

The fermentation indigo vat is still largely used in the East. Meister, Lucius, u. Brüning has a patent for ensuring its more regular action by the use of selectively bred strains of bacteria.¹⁵¹

The thioindigo dyes have been the subject of an interesting series of patents by R. Herz and Cassella u. Co., originating in the discovery of the peculiar reaction between the dry salts of primary amines and sulphur chloride (S_2Cl_2).¹⁵² This subject has been referred to in a previous report, but the publication of the German patents now helps to make the matter a little clearer. Whatever may be the constitution of the new condensation product, it is easily decomposed into an *o*-aminoarylmercaptan,¹⁵³ from which it is clear that the substance obtained from it by the action of alkali and chloroacetic acid is an *o*-aminoarylthioglycollic acid,¹⁵⁴ $NH_2.R.SH \rightarrow NH_2.R.S.CH_2.COOH$. This substance is diazotised, and converted to the nitrile, which on treatment with sodium sulphide or hot alkali forms a ring compound. The latter loses NH_3 and CO_2 when heated with dilute acid and the leuco compound of a vat dye results. This is oxidised by air or oxidising agents, such as ferricyanide, to the dyestuff.

The dyes obtained as a result of this series of reactions are stated to be different from the dyes of the thioindigo series, being brighter and faster than the latter. The dye obtained from aniline, for example, is yellower in shade and faster than Thioindigo Red, while the pink dye from *o*-toluidine is stated to excel all known pink vat-dyes in purity and fastness.¹⁵⁵ *m*-Xylidine gives a bluish-pink dyestuff possessing even better properties than the dye from *o*-toluidine.¹⁵⁶

Ortho- and *para*-aminophenols pass through the series of reactions outlined above, but in this case it is recommended to convert the aminoarylthioglycollic acid into its anhydride by treatment with mineral acid, and brominate it in this form. The bromo compound is then converted through its diazo, nitrile, etc., to a vat dyestuff as before. *p*-Phenetidine thus gives a scarlet vat-dye.¹⁵⁷

¹⁵⁰ Ber., 1922, 55, 3688; 1923, 56, 2027.

¹⁵¹ E.P. 205,834.

¹⁵² G.P. 360,690, 367,344, 367,345. See also E.P. 17,417 of 1914, and Ann. Repts., 1921, 6, 109.

¹⁵³ G.P. 367,346.

¹⁵⁴ G.P. 364,822.

¹⁵⁵ G.P. 367,493.

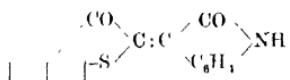
¹⁵⁶ G.P. Appl. C.27,367, C.27,408.

¹⁵⁷ G.P. 371,258.

How the new dyes can differ chemically from the corresponding thioindigo dyes made by the older processes is not clear; in fact it would appear that the differences observed are essentially a matter of purity of the final product.

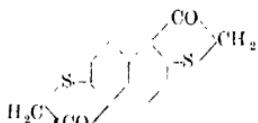
Dyes derived from β -thionaphthisatin are described by the Soc. Chem. Ind. in Basle. This substance is made by condensing β -thionaphthol with oxalyl chloride. It condenses with cyclic compounds containing a reactive methylene group to give vat dyes; thus with oxythiomaphthene it gives a red, with indoxyl a violet, with phenylmethylpyrazolone a brown, with α -naphthol a grey, etc. The new dyes may be brominated.¹⁵⁸

New dyes of the indirubin series have been obtained by F. Bayer u. Co. by condensing 2,1-naphtho-oxythiophene with isatin or an equivalent cyclic α -diketone. For example the dyestuff



is stated to be a brown, fast to light, washing, and chlorine.¹⁵⁹

Thioindigo dyes which have thiophene residues combined twice on a central naphthalene ring are obtained by Kalle u. Co. from naphthalene-dithioglycollic acids by converting them to naphthalene-bisoxothiophenes, e.g.,



which are then condensed with cyclic α -diketones; thus 5-chloroisatin gives a brown vat dye.¹⁶⁰

Vat dyes analogous to Alizarin-indigo but derived from naphthoisatin, e.g., by condensing it with α -naphthol or α -anthrol, when chlorinated with sulphuryl chloride undergo a deepening of shade. Thus, F. Bayer u. Co. claims to obtain a deep bluish-black vat dye by chlorinating the condensation product of β -naphthoisatin chloride and α -anthrol.¹⁶¹

It will be noticed that apart from the new indigo dyeing process and the new light on Cassella's sulphur chloride reaction, the technical interest in the indigoid group of dyes is maintained almost entirely by the naphthoisatin developments. One other patent has appeared during the year which should be mentioned, though the dyestuffs described are probably of a hybrid character and may contain other nuclei than those of an indigoid type.

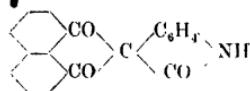
¹⁵⁸ E.P. 186,859, 189,782.

¹⁵⁹ E.P. 198,415.

¹⁶⁰ E.P. 202,734.

¹⁶¹ E.P. 205,790.

Kalle u. Co. obtain a blue vat dye by the alkali fusion of the condensation product of naphthalic anhydride and oxindol,¹⁶² i.e.,



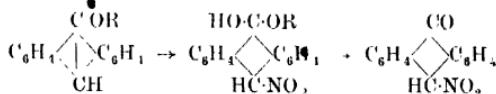
ANTHRAQUINONE DYES.

A new process for the purification of raw anthracene by crystallisation from an alkylated aromatic amine (e.g., dimethylaniline) is claimed by J. Michael & Co. to give pure anthracene of m.p. 213° in one operation.¹⁶³

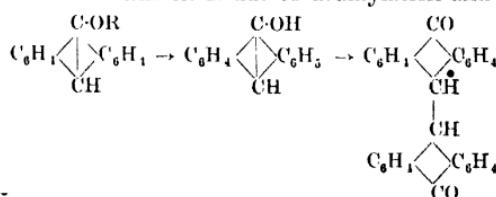
The newer methods of preparing anthraquinone by catalytic oxidation are referred to under "Catalysis." A. Wohl and the Barrett Co. still continue to publish patents in connexion with the vanadium process, while the Chem. Fabr. Worms A.-G. is interested in the oxide of nitrogen process.

By acting on anthracene with chlorine and pyridine H. Hopff and the Badische Co. have obtained 9,10-dihydroanthracene-dipyridinium chloride. This substance loses pyridine and gives pure anthrone on boiling with water.¹⁶⁴

E. de B. Barnett, M. A. Matthews, and J. W. Cook have described methods for the preparation of anthrone, dianthrone, dianthranol, dianthaquinone, and dianthranyl derivatives. A series of chloro-anthrones have been prepared in a pure state by reduction of the corresponding chloroaanthraquinones. The chloroaanthrones were oxidised to dianthrones, but only in certain cases could they be reduced and undergo pinacol condensation to give dianthryl derivatives. The first action of nitric acid on anthrone and anthranol derivatives is an addition at the "bridge" bond, with subsequent change to a dianthrone or a nitroanthrone; thus in the case of anthranyl ethers.¹⁶⁵



The formation of dianthrone is due to dealkylation and oxidation.



¹⁶² G.P. 366,097.

¹⁶³ G.P. Appl. M.75,440.

¹⁶⁴ G.P. 381,180.

¹⁶⁵ *Chem. Soc. Trans.*, 1923, **123**, 230, 1994, 2549, 2631.

A. G. Perkin and his collaborators are engaged in a systematic study of the reduction products of the hydroxyanthraquinones. Several of the latter have been reduced to hydroxyanthracenes, using an aluminium-mercury couple and ammonia. Anthragallol was reduced with stannous chloride to an anthranol, which may have the constitution of 1,2,3-trihydroxy-9-anthrone.¹⁶⁶

The disulphonation of anthraquinone is inefficient, because in addition to the required $\alpha\alpha$ -disulphonic acids, quantities of useless $\alpha\beta$ -acids are produced. J. Thomas and Scottish Dyes, Ltd., propose to hydrolyse these with acid (in the presence of mercury) and thus recover the useful β -monosulphonic acid.¹⁶⁷

Salts of anthraquinonesulphonic acids with arylamines and other bases are described by A. G. Perkin and W. G. Sewell. These salts crystallise well and are generally sparingly soluble. Their use is suggested for the purification and separation of the isomeric anthraquinonesulphonic acids and also for the analytical control of the progress of sulphonation.¹⁶⁸

The preparation of 1-chloro-2-acylaminoanthraquinone by the action of sulphuryl chloride on β -acylaminoanthraquinone is patented by E. Kopetschni.¹⁶⁹ The same author has claimed the production of α - and β -nitroanthraquinones by oxidising the corresponding amines by means of persulphuric acid.¹⁷⁰

In connexion with the amidation of α -anthraquinonesulphonic acid to α -aminoanthraquinone the Soc. Chem. Industry in Basle claims the use of a sulphonic acid of an aromatic nitro compound as oxidising agent.¹⁷¹ The same firm patents the manufacture of 2,3-diaminoanthraquinone by heating 2-amino-3-bromoanthraquinone with ammonia.¹⁷²

β -Chloroanthraquinone has been synthesised from phthalic anhydride and monochlorobenzene. H. Dodd, W. C. Sprent, and the United Alkali Co. now find that *o*-dichlorobenzene gives the same product, one chlorine group being displaced. *p*-Dichlorobenzene is not acted upon under the conditions employed.¹⁷³

4-Hydroxy-1,2-dimethylanthraquinone has been synthesised from phthalic anhydride and 4-*o*-xylenol by A. Fairbourne and J. M. Gauntlett.¹⁷⁴

A new reaction of wide application has been discovered by the

¹⁶⁶ *Chem. Soc. Trans.*, 1923, **123**, 2029, 2603.

¹⁶⁷ E.P. 200,851.

¹⁶⁸ *J.*, 1923, 27T.

¹⁶⁹ G.P. 376,471.

¹⁷⁰ G.P. 363,930.

¹⁷¹ G.P. Appl. G.53,595.

¹⁷² E.P. 203,051.

¹⁷³ E.P. 204,528.

¹⁷⁴ *Chem. Soc. Trans.*, 1923, **123**, 1137.

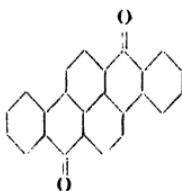
Soc. Chem. Industry in Basle, aminoanthraquinones being condensed with halogenated derivatives of 1.3.5-triazine, e.g., cyanuric chloride. The new products contain more or less chlorine, according to the degree of condensation, the end products of the reaction being free from chlorine and constituting vat dyes. Thus α -aminoanthraquinone gives with cyanuric chloride a yellow dye, and with 2.4-diphenyl-6-chloro-1.3.5-triazine a dark orange, while 4-amino-2.1-anthraquinoneacridone gives with cyanuric chloride a greenish-blue dye. A very wide range of examples is given in the patent.¹⁷⁵

The condensation of aminoanthraquinones with the sulphonochloride of salicylic acid is patented by J. Baddiley, W. W. Tatum, and the British Dyestuffs Corporation, Ltd. The products obtained are acid dyes which dye wool in bright shades, fast to milling and to light, and which may be after-chromed with a little increase in fastness. The new dyes also show good affinity for acetyl silk.¹⁷⁶

The only other discovery relating to acid dyes of the anthraquinone series published during the past year is that of F. Bayer u. Co. for the production of blue to black wool dyes, by sulphonating amino- or alkylaminodianthaquinonylamines. For example, 4.4'-diamino- α , α' -dianthaquinonylamine on sulphonation gives a product stated to dye wool bluish-grey shades, fast to light and milling.¹⁷⁷

A new method of amidating dibenzanthrone by treating the latter with hydroxylamine has been discovered by the Badische Company. The new aminobenzanthrones do not dye green, like the amino compounds previously produced by nitration and reduction of dibenzanthrone, but dye in grey to blue-black shades from the vat.¹⁷⁸

New derivatives of benzanthrones, obtained by condensation with aromatic acid chlorides, are patented by Meister, Leucius, u. Brüning. Thus benzanthrone gives with benzoyl chloride an orange-yellow vat dye having possibly the constitution¹⁷⁹



¹⁷⁵ G.P. Appl. G.56,505.

¹⁷⁶ E.P. 201,610.

¹⁷⁷ E.P. 201,575.

¹⁷⁸ E.P. 204,241.

¹⁷⁹ E.P. 205,502.

The Badische Company has discovered that the conversion of benzanthrone and its derivatives to dibenzanthrones can be made to take place in two stages. The intermediate compounds are formed by mild action of alkaline condensing agents (alcoholic potash, sodium anilide, etc.) and are not dyestuffs, but can be converted to the known dibenzanthrone vat dyes by heating with condensing agents. If the latter have also a halogenating action, e.g., ferrie chloride, halogenated vat dyes result. If fuming sulphuric acid is used sulphonated products can be obtained (e.g., dibenzanthronesulphonic acid) which are converted by oxidation followed by mild reduction to substances giving greenish-blue vats from which cotton is dyed in green shades.¹⁸⁰

The Badische Company also has a patent for condensing an aldehyde or equivalent substance with the products obtained from dibenzanthrone by oxidation followed by mild reduction (hydroxydibenzanthrones). The products described are reddish-blue vat dyes.¹⁸¹

A. H. Davies, R. F. Thomson, J. Thomas, and Scottish Dyes, Ltd., have an interesting patent covering a series of alkylated or acylated hydroxy derivatives which is an extension of their earlier patent¹⁸² for vat greens obtained by alkylating hydroxydibenzanthrones. The hydroxy-compounds covered in the present patent are defined generally as being derived from "ketonic-perlylenes"; that is to say they are the oxidation products of dibenzanthrone, isodibenzanthrone, dimethylbibenzanthrone, dinaphthodibenzanthrone, and dinaphthalimide, all of which contain the perlylene ring system. These oxidation products are converted by mild reduction to substances which are themselves vat dyes, and which can be made still more valuable by alkylation or acylation.¹⁸³

Attempts have recently been made to develop technical methods for the manufacture of perlylene itself, and to use it as an intermediate in the manufacture of vat dyes. According to the claims of H. Pereira, the starting point is β -dinaphthol (2,2'-di-hydroxy-1,1'-dinaphthyl) or its alkyl ether; this is treated with ring-closing agents to form 1,12-dihydroxyperylene,¹⁸⁴ which is then converted into perylene by energetic reduction, for example, by heating with zinc dust.¹⁸⁵ Perylene may be converted by

¹⁸⁰ E.P. 203,533.

¹⁸¹ E.P. 206,638.

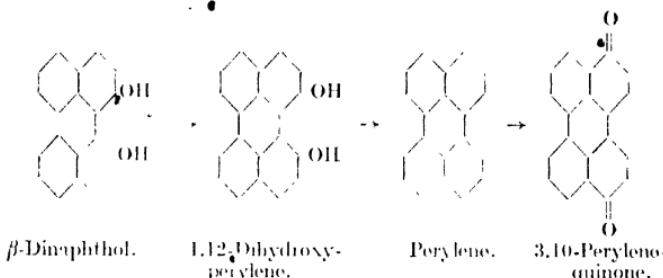
¹⁸² E.P. 181,304.

¹⁸³ E.P. 193,431.

¹⁸⁴ E.P. 191,363, 165,771; G.P. Appl. P.41,931.

¹⁸⁵ E.P. 199,401, 165,770; G.P. Appl. P.41,930.

oxidation by means of chromic acid into 3,10-perylene-quinone. The whole series of reactions is illustrated as follows :—



The 3,10-perylene-quinone can also be obtained directly from 4,4'-dihydroxy-1,1'-dinaphthyl by ring closure, and air oxidation of the resulting 3,10-dihydroxyperylene. This quinone dyes cotton yellow from a red vat.¹⁸⁶ It is claimed that its chloro-derivative dyes cotton in shades which are greener and brighter than the previously known bromo derivatives.¹⁸⁷

Another vat dye giving brown to black shades on cotton is stated to be obtained directly from 1,2-dihydroxyperylene by means of a polysulphide melt.¹⁸⁸

Perylene-quinone can be mono- and di-nitrated, and the dinitro compound is stated to dye cotton in violet shades from the vat.¹⁸⁹ The aminoperylene-quinones obtained by reduction of the nitro compounds are also stated to be vat dyes, the diamino giving violet shades and the bromodiamino violet shades with a brown tinge.¹⁹⁰ More valuable products result from acylating the aminoperylenequinones; thus the monobenzoylamino derivative is stated to dye cotton pink, while the bromodiaminoperylene-quinone benzoylates to give a product dyeing "copper-bronze" shades.¹⁹¹

New vat dyes giving red to blue-violet shades have been obtained by Kalle u. Co. from perylenetetracarboxylic acid by heating it with ammonia, or aromatic or aliphatic amines. The resulting imides are intensely coloured in contrast with the comparatively weakly coloured (orange-yellow) tetracarboxylic acid.¹⁹²

Vat dyes of the anthraquinone series containing sulphur have been rather to the fore during the period under review. Cassella u.

186 E P 206 13 t

¹⁸⁷ E.P. 206,133.

E.P. 200,133.

189 E.P. 197,932.

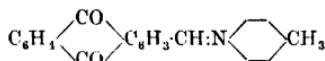
¹⁹⁰ E.P. 199,720.

... E.P. 199,721.

192 G.P. Appl. B

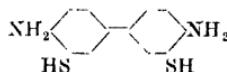
102 G.P. Appl. P.37,769.

Co. have obtained vat dyes ranging from yellow to blue-black by sulphurising the azomethines derived from anthraquinone-2-aldehydes, for example, the compound :—



gives an orange dye; the azomethine from benzidine and 2 mols. of anthraquinone - 2 - aldehyde a brownish - yellow, becoming pure yellow on chlorinating ; the azomethine from *p*-phenylenediamine and 1 - aminoanthraquinone - 2 - aldehyde a violet, etc.¹⁹³ The products are doubtless thiiazoles. The process can be simplified by avoiding the intermediate formation of the azomethine and heating the mixture of an ω -halogen derivative of 2-methylanthraquinone (*e.g.*, the ω -di- or trichloro-derivative) with an aromatic amine and sulphur.¹⁹⁴ A further simplification is the use of 2-methylanthraquinone itself, heated simply with sulphur and an amine, *p*-diamines apparently giving the most useful dyes ; thus 2-methylanthraquinone and benzidine by heating with sulphur give a reddish-yellow vat dye.¹⁹⁵

According to another invention of Cassella u. Co., vat dyes are obtained by heating, alone or with solvents, the azomethines formed from anthraquinone-2-aldehydes and *o*-aminophenols or *o*-aminothiophenols. The dyestuffs are probably oxazoles in the former case and thiiazoles in the latter. The thiiazoles are apparently identical with the dyes obtained by sulphurising azomethines as in the previous paragraph. As before, the most valuable dyes are those derived from *p*-diamines, through their di-*o*-mercapto derivatives. For example, from anthraquinone-2-aldehyde and the substance



(which may be obtained from benzidine by the action of sulphur monochloride) dyes are obtained which are similar to those resulting from the sulphurisation of the condensation product of anthraquinone-2-aldehyde and benzidine.¹⁹⁶

Thiazoles which are isomeric with some of those obtained according to the above patents are described by the Badische Company. They are yellow vat dyes and are obtained by condensing 1-mercapto-2-aminoanthraquinone with an aromatic compound containing as substituents in its molecule at least two reactive carbon

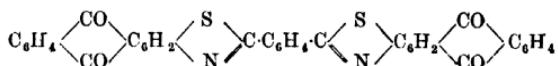
¹⁹³ G.P. Appl. C.25,892.

¹⁹⁴ G.P. Appl. B.98,100.

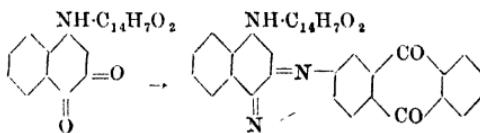
¹⁹⁵ G.P. Appl. C.30,716 ; E.P. 189,367.

¹⁹⁶ E.P. 198,077.

atoms. For example, 2 mols. of 1-mercaptop-2-aminoanthraquinone and 1 mol. of terephthaloyl chloride give¹⁹⁷



A series of new vat dyes has been obtained by the Soc. Chem. Industry in Basle by condensing β -naphthoquinone or its derivatives with α -aminoanthraquinone or $\alpha\alpha$ -diaminoanthraquinones. The products condense readily with σ -diaminoanthraquinone to give vat dyes, e.g., β -naphthoquinone is condensed with α -aminoanthraquinone and the product further condensed with 2,3-diaminoanthraquinone, thus:—



The product illustrated dyes bordeaux shades.¹⁹⁸

The looseness to chlorine of ordinary Indanthrene Blue appears, according to a patent of the Badische Company, to be due to the presence of impurities. A dyestuff free from these impurities, and fast to chlorine, can be obtained by starting out from β -aminoanthraquinone which has been purified by fractional precipitation from solution in strong sulphuric acid. Alternatively, Indanthrene Blue made from the ordinary quality of β -aminoanthraquinone can be purified and made chlorine-fast by fractional precipitation from sulphuric acid solution. Another method of eliminating the objectionable impurity is by prolonging the caustic potash fusion of β -aminoanthraquinone.¹⁹⁹

QUINONE VAT DYES.

This new class of dyes originated about 1911, and was just beginning to be known when the war broke out. The work commenced with the patent of R. Lesser (purchased by Meister, Lucius, u. Brüning) for using as vat dyes the quinone-anilides, such as dianilinoquinone (dyes yellow) and dianilinonaphthoquinone (dyes red).²⁰⁰ This discovery was rapidly developed by Meister, Lucius, u. Brüning, and a stream of patents began to pour out, the main object of which was the improvement in the shade

¹⁹⁷ E.P. 204,249.

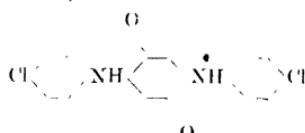
¹⁹⁸ E.P. 195,753.

¹⁹⁹ E.P. 184,193.

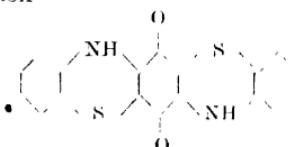
²⁰⁰ G.P. 236,074.

and dyeing properties of the simple quinone-anilides, generally by treating them with sulphurising agents.

The constitution of the new dyes is not quite certain, except in the case of the simplest members of the series, the quinone-anilides, of which a typical example is²⁰¹



The dyes made by sulphurising the quinone-anilides (preferably containing halogen groups in the quinone residues) are probably thiazine-quinones. A typical case is the product of the action of sodium sulphide on the dianilide of dichloroquinone, and it may have the constitution²⁰²



The sulphurisation, according to the examples given in the patents, is probably not very far-reaching as compared with the case of the ordinary sulphide dyes. At the same time, the ultimate shade and dyeing properties of the new dyes are influenced by the conditions of reaction, from which it would appear that, like the sulphur dyes, they are not perfectly homogeneous, and their chemistry must be discussed with caution.

Alternative methods of preparation which have been patented appear to confirm the thiazine-quinone constitution; for example, dyes very similar to the sulphurised chloroquinone-anilides are obtained by the action of arylamines on quinone thio-derivatives such as the thiosulphonic acids, mercaptans, and the diquinone-sulphides and disulphides.²⁰³ The shade of the dyes obtained in this way can be improved (*i.e.*, intensified) by further treatment with an acid (concentrated sulphuric acid) or an acid reducing agent.²⁰⁴

The dyes already referred to all come within the yellow to brown range of shades. An extension in the direction of black is described in a recent patent of Meister, Lucius, u. Brüning, in which the *m*- and *p*-nitroanilides of benzoquinone or halogenated benzoquinone are sulphurised. Thus the condensation product of *m*-nitroaniline

²⁰¹ G.P. 262,180.

²⁰² G.P. 263,382, 265,195.

²⁰³ G.P. 362,457.

²⁰⁴ E.P. 147,704; G.P. 366,734.

and chloranil gives brown-grey to green-grey dyes, according to the conditions of sulphurisation.²⁰⁵

Latterly the same firm has included naphthoquinones within the scope of this series. It has been found that when 2,3-dichloro-4-naphthoquinone is condensed with aniline and the product treated with sodium sulphide, 2-phenylamino-3-mercaptop-1,4-naphthoquinone is formed. This mercaptan readily oxidises in air to form benzonaphtho-*p*-thiazine-quinone.²⁰⁶

The new dyes are particularly adapted to the dyeing of wool from the hydrosulphite vat, and certain marks of Helindone Yellow and Brown may belong to this class. Trouble seems to have been encountered on account of bad vatting properties, however, and many of the later patents of Meister, Lucius, u. Brüning have reference to easily applied leuco-preparations.²⁰⁷ The production of stable, dry preparations of mixed leuco compounds of one or other of the new vat dyes, together with leucoindigo, appears to be particularly interesting. The combination shades produced by such mixtures may range from green to black. A successful vat-dye for wool would compete with the chrome blacks which have hitherto held undisputed sway in the dyeing of fast blacks on this fibre.²⁰⁸

An expansion of the quinone vat dyes literature on lines more or less similar to those originally followed by Meister, Lucius, u. Brüning is now taking place at the instance of other colour firms. Cassella u. Co., for example, condenses a quinone or a halogenated quinone with an *o*-arylamino-mercaptop or an equivalent thereof, such as an *o*-aminoarylthiosulphonic acid, an *o*-diaminodiararyl disulphide, or one of the products of the novel reaction of sulphur chloride on an amine discovered by Cassella u. Co.²⁰⁹ The products obtained dye wool brown from a hydrosulphite vat. From their mode of formation they would be expected to be closely related in constitution to the dyes described earlier by Meister, Lucius, u. Brüning. The patent covers the further treatment of these products with polysulphide, in which case true sulphide dyes are obtained, i.e., they dye cotton from a sodium sulphide bath in shades ranging from red to black.²¹⁰

The products obtained from the arylamides of *o*-quinones differ from those discussed above. Cassella u. Co. have obtained from 3-naphthoquinone, either by condensing it with an *o*-aminoaryl-mercaptop or alternatively by sulphurising its arylamide, dyes which give comparatively uninteresting shades when dyed on wool

²⁰⁵ G.P. 370,155.

²⁰⁶ G.P. Appl. F.49,207.

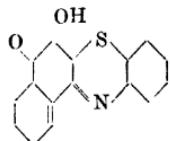
²⁰⁷ G.P. 368,161.

²⁰⁸ E.P. 171,078, 177,526.

²⁰⁹ E.P. 17,417/14, 18,292/14.

²¹⁰ E.P. 204,108. See also Kleinmann's G.P. Appl. K.54,175.

from the vat, but which turn to very fast shades (green) when after-chromed. These dyes may have a simple thiazine structure, e.g.,



and the *o*-hydroxy group would explain the chroming property.²¹¹

In order to round off the review of this group of dyes reference should be made to the vat green obtained by the Badische Company by simply heating α -naphthoquinone with water under pressure.²¹²

A new discovery by the Akt.-Ges. f. Anilinfabr. can be conveniently dealt with under the heading of quinone vat dyes, though what the constitution of the new dyes may be is a matter for speculation. They are prepared by condensing a 1,4-quinone which has a halogen group in the 2-position (e.g., chloranil, 2,3-dichloro-1,4-naphthoquinone, 2,3-dichloro-4-naphthasultamquinone, etc.) with a phenazine or naphthiazine having an -OH or -NH-SC₂-group in a *para*-position to one of the azine nitrogens, e.g., hydroxytoluphenazine (from 2-hydroxy-5-methyl-1,4-benzophenone and *o*-phenylenediamine) or eurhodol (from 2-hydroxy-1,4-naphthoquinone and *o*-phenylenediamine). The new products dye cotton generally in yellow shades from the hydrosulphite vat.²¹³

It has further been found that the hydroxyphenazines or hydroxynaphthiazines mentioned above can be replaced by acridines which have an OH group in the *para*-position to the acridine carbon atom. For example, 2,3-dichloro-1,4-naphthoquinone when condensed with the dihydroxyacridine obtained from 3-amino-1-naphthol and formaldehyde gives a vat brown.²¹⁴

SULPHIDE DYES.

Comparatively few important novelties with regard to sulphide dyes have been announced in the literature in recent years. According to an invention of the Soc. Chem. Ind. in Basle indophenols derived from *p*-aminophenols and monoalkyl- α -naphthylamines are converted into sulphonic acids by treating them with bisulphite. The new sulphonics acids on treatment with polysulphide in the presence of copper give sulphide greens.²¹⁵

A bright greenish-blue sulphide dyestuff is claimed by F. Bayer

²¹¹ G.P. Appl. C.28,296, C.26,297; cf. E.P. 151,000, and *Ann. Repts.*, 1922, 7, 103.

²¹² G.P. 367,689, 350,738; cf. E.P. 168,447; *Ann. Repts.*, 1922, 7, 103.

²¹³ E.P. 192,842.

²¹⁴ G.P. Appl. A. 36,973.

²¹⁵ E.P. 201,540.

u. Co. to be obtained by sulphurising the indophenol obtained from methylbenzylaniline and quinonechlorimide.²¹⁶

Improvements in the manufacture of the carbazole-indophenol dyes (Hydron Blue) are claimed by W. L. Galbraith, W. Lewcock, and S. B. Tallantyre (Gas Light and Coke Co.), the essential feature of which is the formation of the indophenol from carbazole and nitrosophenol by bringing the reagents together at temperatures not exceeding -5°C. The lower the temperature the purer the resulting indophenol. In the case of the alkylcarbazoles the maximum temperature recommended is -10° C.²¹⁷

The Soc. Chem. Ind. in Basle claims that the addition of benzidine has a favourable influence on the sulphur-melt of carbazole-indophenol, a new dye resulting which is more like indigo than that obtained from the carbazole-indophenol alone.²¹⁸

MISCELLANEOUS DYES.

Halogenation of acridine dyes has a beneficial effect especially on the shade.²¹⁹ A. G. Green, E. B. Adams, and the British Dyestuffs Corporation, Ltd., have discovered that acridinium salts can be brominated in cold aqueous solution to give orange to scarlet basic dyes. These dyestuffs, when subjected to the action of acids or acid salts, are again converted into other new products which upon dyeing exhibit a further remarkable change of colour. They produce in dyeing and printing shades of red far bluer than the original bromination products. This change also occurs during bromination if it is effected in the presence of a sufficient amount of a mineral acid. The nature of the transformation has not yet been fully elucidated, but it is believed by the patentees to be due to a molecular re-arrangement involving a transposition from an *ortho*-quinonoid to a *para*-quinonoid type.²²⁰

9-Aminoacridine and its derivatives have been synthesised in various ways by Meister, Lucius, u. Bünning.²²¹

A number of dyes analogous to the phthaleins have been prepared by various investigators. A. Lapworth and J. A. McRee have obtained resorcinolphenylsuccinein by condensing phenylsuccinic acid with resorcinol.²²²

The condensation of diphenic anhydride with resorcinol was found by F. Bischoff and H. Adkins to yield a product very similar

²¹⁶ U.S.P. 1,449,681.

²¹⁷ E.P. 201,624, 201,625.

²¹⁸ E.P. 199,360.

²¹⁹ G.P. 360,604.

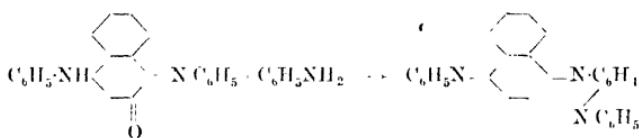
²²⁰ E.P. 194,165.

²²¹ G.P. 360,421, 364,031-7, 367,084.

²²² *Chem. Soc. Trans.*, 1922, 121, 2722.

to fluorescein and which gave a tetrabromo-compound like Eosin.²²³ Pyrrol-phthalein has been described by B. Oddo and F. Tognacchini.

A new synthesis in the azine group has been described by A. Wahl, R. Lantz, and the Soc. Anon. des Mat. Col. et Prod. Chim., St. Denis: 4-arylamino-1-arylimino-2-naphthoquinone (see page 100) is oxidised in the presence of aniline. Phenylrosinduline is stated to be obtained in this way in nearly theoretical yield and pure enough to be sulphonated directly to Azo Carmine.²²⁵ The reaction is as follows:—



A novel type of dyestuff is claimed by I. K. Lehmkedt to be obtained from glycine either by nitration and reduction or by halogenation and amidation.²²⁶

Decacylene and dinaphthylmethiophene (the products of dehydrogenation of acenaphthene by means of sulphur) are stated by K. Dziewonski to give acid dyes when sulphonated. The sulphonic acids give vat dyes when fused with caustic alkalis.²²

Another example of a sulphonated hydrocarbon which gives acid dyes having good tinctorial power is provided by F. Kehrmann and C. Buflat, namely, dibiphenylene-ethane the sulphonic acid of which dyes wool and silk in shades similar to those given by Orange II.²²⁸

²²³ *J. Amer. Chem. Soc.*, 1923, **46**, 1030.

²²⁴ *Gazz. Chim. Ital.*, 1923, **53**, 265.

225 E.P. 206,488.

²²⁶ G.P. Appl. L.53,695, L.53,697.

227 G.P. 379,616, 385,956.

²²⁸ *Helv. Chim. Acta*, 1923, 6, 955.

FIBRES, TEXTILES, CELLULOSE, AND PAPER.

By CHARLES DORÉE, M.A., D.Sc., F.I.C.,

Chemistry Department, Borough Polytechnic Institute, S.E.

THE year 1923 has been one of steady progress in the development of our knowledge of the chemistry and technology of textiles, particularly of those based upon cellulose. On the chemical side the work of the St. Andrews school has finally resulted in a constitutional formula for the cellulose unit complex and paved the way to a future synthesis of cellulose. The British Cotton Industry Research Association, on the other hand, has initiated a series of researches into the physical and technical qualities of the cotton hair—the unit on which all the qualities of cotton as a structural material are founded, which will ultimately prove of the greatest technical value. Both sides, the chemical and the physical, are of fundamental importance; yet it is interesting to note in going through the literature that at present they are almost completely divorced from one another. A knowledge of the chemical constitution of cotton cellulose does not yet help in the manifold applications of the cotton hair, and an insight into the composition of lignin does not explain the qualities of wood as a structural material.

COTTON.

Raw Cotton : Supply and Preparation.

W. R. Donop¹ has considered the problems connected with the supply of raw cotton, pointing out that during the past twenty-five years the consumption has been increasing at a greater rate than production, this being due partly to the decline in the average crop per acre in Egypt and America, and partly to the pink boll worm in Egypt and the cotton boll-weevil in the States. The report of the British Cotton Growing Association states that the number of bales marketed by them from African and other sources constituted a record both in number and value. It points out incidentally the increase in the consumption of home-grown cotton by American mills from 36% in 1901 to 55% in 1922. It is satisfactory to note that the Council of the Textile Institute has undertaken² the promotion of the Empire Textile Conference at

¹ *J. Text. Inst.*, 1923, **14**, 157p.

² *Ibid.*, 1923, **14**, 169p.

the British Empire Exhibition of 1924. The scientific investigation of cotton in the widest sense will undoubtedly take a prominent place in the deliberations of this Conference.

The University of Manchester is co-operating with the Empire Cotton Growing Association in a campaign against the parasites, animal and fungoid, which attack cotton. As a beginning, three highly qualified investigators have been appointed to carry out research.

The question of cotton grading in the United States is considered in several articles.³ The United States Cotton Standards Act contemplates the issue of regulations (*a*) for the classification of samples with a view to enable an owner to obtain the commercial value of the samples, and (*b*) the collection and classification of samples of undoubted authenticity. The official samples are stored in evacuated tubes under special conditions, of which a description is given. The certificate of the Department of Agriculture is to be the final word as to classification for legal purposes.

H. Flühr⁴ describes a number of new methods for determining mean staple lengths and constructing staple diagrams. In a typical one a sliver, in which the hairs are well mixed and paralleled, is gripped along a line at right-angles to its length. The loose hairs are combed out, the sliver is cut along the line of grip, and the tuft weighed. The mean staple length is then given by the product of $2 \times$ length per unit mass of sliver \times mass of the tuft.

The question of softening the cotton wax in the preparation of cotton is dealt with by P. F. Estey,⁵ who gives directions for the preparation of a number of softening mixtures, and by E. Knecht,⁶ who recommends the treatment of dry cotton, at any stage up to the spinning process, with air charged with the vapour of such hydrocarbons as solvent naphtha.

The importance of the incrusting materials present in raw cotton has long been recognised both from a technical and a scientific point of view, and we note considerable progress in the elucidation of their nature and relationships. Working on lines which have proved so successful in the examination of many plant materials, R. G. Fargher and E. M. Probert,⁷ of the British Cotton Industry Research Association, examined the benzene extract from two tons of American cotton sliver, the 8 lb. of solid wax obtained being extracted fractionally with solvents. The major constituent of the wax is a new alcohol, $C_{30}H_{62}O$, to which the name of gossypyl alcohol is given. It occurs in three forms, differing in

³ *Text. World*, 1923, **64**, 228, 265.

⁴ *L'Ind. Text.*, 1923, **39**, 156.

⁵ *Amer. Dyestuff Report*, 1922, **11**, 300.

⁶ E.P. 195,870; *J.*, 1923, 545A.

⁷ *J. Text. Inst.*, 1923, **14**, 49T; *J.*, 1923, 263A.

melting point and solubility: the γ -form, m.p. 87°, appears in the petroleum ether extract; the α -form, m.p. 87°, which is the most insoluble of the three, is found in the chloroform extract. The other constituents include montanyl alcohol, $C_{28}H_{58}O$, and carnaübyl alcohol, together with phytosterol and sitosterol (the latter as glucoside). The hydrocarbons, $C_{39}H_{62}$ and $C_{31}H_{64}$, were isolated, together with a mixture of liquid hydrocarbons of the approximate composition C = 86.6%; H = 12.8%.

S. H. Higgins⁸ urges greater uniformity in the methods employed in the analytical extraction of vegetable fibres by solvents. He suggests, as a standard, extraction with benzene for 8 hours. This author finds that extraction with any particular solvent is incomplete. A sample of flax, for example, which gave 1.39% of wax when extracted with ether, gave a further 0.27% on extraction with benzene. These results probably find an explanation in the observations (described above) on the varying solubility of the three forms of gossypyl alcohol.

E. Knecht and G. H. Streat⁹ have also critically examined these points, working with considerable quantities of Egyptian, Indian, Nigerian, and American cotton. They find generally that after partial mechanical or chemical disintegration all cottons give a higher percentage of extract to organic solvents such as benzene. Thus an American cotton completely exhausted with benzene gave 0.63% of extract. It was then treated for 15 minutes with hydrochloric acid of sp. gr. 1.02, after which a further 0.21% of extract was obtained. Further treatment with acid of sp. gr. 1.025, boiling for 15 minutes, drying and powdering, resulted in the extraction of an additional 0.39% of waxy matter. A crystalline solid, m.p. 62°, was isolated from these (? palmitic acid); and from Egyptian cotton, besides the cotton wax of Schunk, m.p. 86°, another substance of m.p. 79° was obtained.

A process for the partial removal of incrusting matters from cotton yarn by extraction with gasoline and other solvents, whereby an increase in tensile strength of upwards of 25% is claimed, forms the matter of a patent by R. W. Jacoby.¹⁰

A further notable contribution to our knowledge of the reactivity of the substances associated with raw cotton, results from the experiments of P. H. Clifford and R. G. Fargher,¹¹ who have examined the volatile products obtained by the hydrolysis of American cotton (a) with 2% sodium hydroxide solution, and (b) with water alone, under a pressure of 40 lb., for 8 to 10 hours in each case. Among nitrogenous substances ammonia and tri-

⁸ *J. Soc. Dyers and Col.*, 1923, **39**, 150; *J.*, 1923, 599A.

⁹ *Ibid.*, 1923, **39**, 73; *J.*, 1923, 345A.

¹⁰ U.S.P. 1,398,378; *J.*, 1923, 493A.

¹¹ *J. Text. Inst.*, 1923, **14**, 117T; *J.*, 1923, 709A.

methylamine were isolated by both methods, while the alkali treatment gave also a pyrrole derivative. The alkaline treatment gave as chief products methyl alcohol and acetone, whereas with water alone acetaldehyde and acetone were obtained. A number of other products of an aldehydic or ketonic character were isolated in derivative form. A minute quantity of an oil was also found from which an aldehyde or ketone, $C_{10}H_{20}O$, could be separated, the remainder consisting of an oil of camphoraceous odour which darkened on keeping and proved highly resistant to all the usual chemical reagents. Its analytical composition ($C = 82\cdot6\%$: $H = 11\cdot25\%$) pointed to the formula $C_{19}H_{30}O$.

Structure and Properties of the Cotton Hair.

R. O. Herzog¹² continues his interesting researches on the X-ray structure of cellulose, which show that the ultimate elements of the hair consist of minute crystals, one axis running parallel to the length of the fibre. The British Cotton Industry Research Association has during the year contributed a number of valuable papers dealing with the cotton hair—a unit the fundamental importance of which was early recognised by W. L. Balls. It is rightly insisted that the term "cotton hair" is to be preferred to that of "cotton fibre," and the former term will be adopted in all communications of the Association. The papers themselves which are illustrated by numerous plates, are exceedingly difficult to summarise and nothing more than an indication of their contents can be given. H. J. Denham¹³ continues his study of the structure of the cotton hair and its botanical aspects, considering now the morphology of the wall. The work contains 86 photographs and a valuable appendix is included dealing with optical fallacies and errors due either to incorrect adjustment of the microscope or to images formed with polarised light. The structures involved in the wall of the cotton hair are described under the headings of striations, convolutions, slip-planes, Mosenthal's pits, "buckling" lines, and abnormalities. The slip-planes shown by Robinson to occur in the cell walls of strained wood are found to occur widely in cotton. The author is able finally to give a tentative theory of wall formation.

W. L. Balls¹⁴ has devised three new methods for the examination of the structure of the hair, *viz.* (a) observation in elliptically polarised light, (b) preparation of longitudinal sections, (c) the development in the primary wall of a definite structure and of a substance reacting to cellulose stains, by boiling with potassium hydroxide solution. The results obtained by the application of

¹² *Chem.-Ztg.*, 1923, **47**, 21.

¹³ *Shirley Inst. Mem.*, 1923, **2**, 61.

¹⁴ *Proc. Roy. Soc.*, 1923, **B95**, 72.

these methods are of the highest interest, and in addition to the structural elements determined, various chemical relationships are indicated. For example, the effects of certain structures on polarised light are scarcely affected by strong alkalis, yet are abolished by acids. Speculations as to the ultimate structure in terms of the space lattice hypothesis are given, and the author suggests that the wall is a sponge-like structure with free air-spaces in between. The specific gravity of the cellulose cell-walls is about 0·9-1·1. An interesting lecture, including a discussion of many of these difficult problems, was given by W. L. Balls¹⁵ at the meeting of the British Association at Liverpool.

The rigidity of cotton hairs has been examined by F. T. Peirce,¹⁶ who shows that the resistance to twist and the forces developed during the twisting of a cotton hair, have a direct influence on yarn properties. The coefficient of rigidity was found to be $0\cdot23 \times 10^{11}$ dynes per sq. cm. (about one-tenth of that of glass). Hairs of all kinds are shown to have an approximately constant volume of cellulose which is independent of the staple length. For normal hairs this volume is $3\cdot8 \times 10^{-6}$ c.c. There are thus about $4\cdot25 \times 10^6$ hairs to the cubic inch, or $78\cdot5 \times 10^6$ to the pound of cotton. Another piece of work by the same author¹⁷ deals with the plasticity of cotton hairs and other textile materials. The work was undertaken to study the effect of time and temperature conditions, and of humidity, on the twist in yarns. The method described, however, is of much wider application and may be used to determine the optimum conditions and efficiency of such major operations as spinning, maturing, doubling, and finishing, and also of textile qualities affecting the handle, the recovery after stretching, creasing, sagging, and the effects of washing and ironing. A magnetic torsionmeter employed is fully described and illustrated.

On similar lines the physical and structural conditions accompanying the mercerisation of single cotton hairs have been studied by R. S. Willows, T. Barratt, and F. H. Parker.¹⁸

These observations, published in 1922, and dealing more especially with the influence of the alkaline solutions on the length and cross-section of the hairs, have been supplemented by those of G. E. Collins and A. M. Williams¹⁹ on the swelling of the cotton hair in aqueous solutions. The change in length of the hairs is measured by an instrument on the lines of J. Mueller's turgometer. The increase in length observed in water and dilute solutions of alkalis is due almost entirely to the removal of convolutions, and therefore the more complete their removal in preliminary treat-

¹⁵ *J. Text. Inst.*, 1923, **14**, 202T.

¹⁶ *Ibid.*, 1923, **14**, 1T.

¹⁷ *Ibid.*, 1923, **14**, 390T.

¹⁸ *Ibid.*, 1922, **13**, 229; *J.*, 1923, 51A.

¹⁹ *Ibid.*, 1923, **14**, 287T, 264T; *J.*, 1923, 1066A.

ments, the greater will be the shrinkage of the hairs in the mercerisation process. Maximum swelling occurs at a 15% solution of sodium hydroxide, and no advantage is gained by increasing the concentration beyond this point. H. F. Coward and L. Spencer²⁰ have also contributed valuable observations to this problem of swelling. With the aid of a suitable centrifuge working up to 8000 revolutions per minute, they have made the first direct determinations of the water and sodium hydroxide present in the alkali-saturated cotton. No evidence of chemical combination between alkali and cellulose, nor of simple adsorption, was obtained. Maximum swelling, in agreement with the work described above, was found at 14.3% sodium hydroxide, from which it is deduced that it is the cuticle which limits the swelling. The maximum swelling is less with yarns and fabrics, owing to the additional constraint imposed. The results also emphasise the necessity of keeping the cloth under tension till nearly all the mercerising alkali is removed.

The Action of various Agents on Cotton.

A. M. Williams,²¹ in a note on the compression of cotton for experimental purposes, mentions that although theoretically 15 grams of cotton should go into a 10-c.c. tube, in practice no more than 2.5 grams can be inserted. By using a screw pastille press, however, plugs of cotton can be made so that as much as 7 grams can be handled in a 10-c.c. tube. The mechanical breakdown of a cotton driving rope under acute bending previously referred to²² has been considered by W. Warr²³ as evidence that permanent change in the reactivity of cotton can be induced by mechanical means, and he has utilised these observations in a most ingenious way. The author finds that if a piece of wet calico stretched on a glass plate is subjected to pressure, e.g., by drawing the end of a glass rod over it, the marks will be seen when the cloth is dyed with a vat, sulphur, or direct cotton colour. The effect is not removed by bleaching, and on such pressure-patterns a new method for ornamenting cotton and other fabrics has been based, the process for which is awaiting commercial exploitation.

A useful review of the literature surrounding the action of light on cotton is given by P. W. Cunliffe.²⁴ P. Waentig²⁵ has studied the action of a 1500 H.K. quartz-mercury lamp on cotton, as well as on most other textile fibres. If the light were passed first

²⁰ *J. Text. Inst.*, 1923, **14**, 28T, 32T; *J.*, 1923, 221A.

²¹ *Shirley Inst. Memoirs*, 1923, **2**, 225.

²² Cross and Dorée, "Researches on Cellulose," 1922, pp. 17, 18.

²³ *J. Soc. Dyers and Col.*, 1923, **39**, 361.

²⁴ *J. Text. Inst.*, 1923, **14**, 314T.

²⁵ *Z. angew. Chem.*, 1923, **36**, 357; *J.*, 1923, 825A.

through a sheet of ordinary or Uviol glass it had no action. The author disputes Turner's statement that the destructive effect is one of oxidation, since no oxycellulose could be found in the exposed cotton, and the tendering took place also in an atmosphere of nitrogen. These results, it may be mentioned, are at variance with those previously obtained by the present writer and others.

The relation of the moisture content of cotton and other textile materials to the humidity of the surrounding atmosphere has been studied by R. E. Wilson and T. Fuwa,²⁶ who have given curves from which the humidity equilibria have been obtained under a variety of conditions. The moisture content rises slowly in air possessing a low humidity, say, between 20 and 60%. Linen shows a minimum moisture-content at a maximum humidity.

The qualitative and quantitative absorption of Methylene Blue by cellulose fibres has for many years been employed as a general test for "oxycellulose" and over-bleaching. As a prelude to an attempt to determine more exactly the relation between the extent of oxidation and the amount of dyestuff absorbed by the cotton, C. Birtwell, D. A. Clibbens, and B. P. Ridge²⁷ have studied the absorption of Methylene Blue by normal cotton celluloses. The paper should be consulted for several useful points of technique. The results obtained by titration with Naphthol Yellow S. and by the titanous chloride method agreed closely. Examination of the usual colorimetric method showed that it is incorrect to assume, as is usually done, that the concentrations of two solutions of Methylene Blue showing equal colour intensity are inversely proportional to the observed lengths of the columns of solution. If the concentrations of standard and unknown are considerably different this assumption is very far from the truth. The authors find that in order to avoid this error solutions of 20 mm. depth for the standard should be matched by unknown solutions of between 17 and 23 mm. in depth.

The general results show that the absorption varies with the origin of the raw material, e.g., American cottons have a lower absorption than Egyptian samples bleached in the same way. The absorption varies also, as stated originally by Rona and Michaelis, with the ash content, or rather the ash alkalinity. If the cotton remains the same the decrease in absorption follows the removal of the non-cellulosic impurities, and hence the Methylene Blue test does offer a method of following the progress of the removal of such impurities during bleaching.

The action of micro-organisms on cellulose continues to be examined from the two points of view: (1) the nature and pre-

²⁶ *J. Ind. Eng. Chem.*, 1922, **14**, 913.; *J.*, 1922, 925A.

²⁷ *J. Text. Inst.*, 1923, **14**, 297T; *J.*, 1923, 1066A.

vention of their attack on the fibres, and (2) the fermentation of cellulose for the production of power gas and other products.

H. J. Denham²⁸ in a communication illustrated by many photomicrographs of damaged fibres, shows that serious damage may exist in cotton before any indication can be obtained by the usual methods, and that even localised infection may seriously interfere with spinning qualities.

From the chemical side C. Neuberg and R. Cohn²⁹ find that when fermented at 37° or 55° C., cellulose, in breaking down to hydrogen and methane, yields acetaldehyde as an intermediate product, the process thus resembling a butyric acid fermentation. H. Langwell and H. L. Hind,³⁰ whose work on the production of power-gas from cellulose is well known, contribute a paper to the Institute of Brewing, in which they point to the 12,000 tons of spent hops annually available in this country as a waste cellulose. The great defects in the application of the cellulose-fermenting organism used by these workers lie in its extreme sensitiveness to traces of copper and in the fact that it cannot decompose cellulose in the presence of unaltered lignin, although all non-lignified celluloses are readily attacked.

The report of a discussion on the fermentation of cellulose, initiated by the Society of Chemical Industry,³¹ contains contributions by well known authorities in this field, whilst an excellent review of previous work on the action of micro-organisms on cotton and cotton fabrics is given by D. Arnstead and S. C. Harland.³²

A variety of agents, chemical and mechanical, are brought to bear on cellulose fibres in the course of the ordinary laundry process in which treatment with dilute alkaline solutions in the presence of air and oxidising agents is constantly repeated. The effects have never been studied, but a few tentative publications that have recently appeared show that the subject is attracting attention. The British Launderers' Research Association also has a scheme of research in hand dealing with these points, the results of which will be awaited with interest.

WOOL.

The British Research Association adopts a sound policy by instituting a series of Research Fellowships and advanced Scholarships for work in connexion with the woollen and worsted industries. The first appointment is in connexion with the investigation of the action of fungi on wool during storage.

²⁸ *J. Text. Inst.*, 1922, **13**, 240; *J.*, 1923, 49A.

²⁹ *Biochem. Zeits.*, 1923, **139**, 527; *J.*, 1923, 903A.

³⁰ *J. Inst. Brewing*, 1923, **29**, 302; *Chem. and Ind.*, 1923, 237.

³¹ *J.*, 1923, 279T.

³² *J. Text. Inst.*, 1923, **14**, 157T.

The Department of Agriculture, U.S.A., is endeavouring to secure uniformity in the use of wool trade definitions between the English-speaking peoples. A representative set of samples, graded according to the Bradford system, has been collected and verified by the Topmaking Committee of the British Wool Federation for the use of the Washington Department in this connexion.

An interesting account of the Government Wool-disinfecting Station at Liverpool³³ states that the introduction of a scheme for the compulsory disinfection of wool gave rise to much uncertainty and apprehension in the trade, leading to a fall in imports. Confidence is, however, now restored, and since June last the station has been constantly employed. The process includes two mild alkaline soap baths, followed by treatment with formalin.

The new conditioning house at Bradford, described in a recent article,³⁴ employs a current of dry air at 112° C., the sample being weighed at intervals on a travelling balance. The tests are complete in 45 to 60 minutes.

S. A. Shorter³⁵ discusses the moisture content of wool from the point of view of scientific theory in relation to commercial practice. He severely criticises Hartshorne's work on the equilibrium between wool and atmospheric moisture, showing that the older work of Schloesing is far more accurate. Curves are given which show that for rapid conditioning high humidity and not too low a temperature are needed. Milling, according to the author, is primarily due to the fact that wool fabric under proper conditions of fibre contact becomes a collection of self-tightening mechanisms. High humidity is considered to act deleteriously by increasing the extensibility of the fibres, and on these lines the bad effect of high humidity in spinning English rovings is explained.

E. A. Fisher³⁶ also contributes a study of the rates of evaporation of water from wool, sand, and clay. Curves are given showing the variation in evaporation-rate as the water content falls. It is concluded that the forces which cause the water to be retained are similar in each of the colloidal systems examined, and that the shrinkage of wool is a deformation and not a volume shrinkage.

The production, for special effects, of a wool yarn which, on moistening, shrinks considerably, is claimed by H. J. W. Bliss and the British Research Association for the Woollen and Worsted Industries.³⁷ The yarn is wetted, stretched to an increase of at least 8% in length, and dried under tension. If exposed during tension to moist heat the stretching effect is permanent.

³³ *Chem. and Ind.*, 1923, 199.

³⁴ *Textile Recorder*, 1923, **40**, 65.

³⁵ *J. Soc. Dyers and Col.*, 1923, **39**, 270; *J.*, 1923, 1017A.

³⁶ *Proc. Roy. Soc.*, 1923, **A103**, 139; *J.*, 1923, 479A.

³⁷ E.P. 190,881; *J.*, 1923, 179A.

S. v. Kapp³⁸ has made an exhaustive examination of the action of various chemical and physical treatments on woollen fabrics. He states that the wearing test is far more sensitive than the tensile strength measurement.

The effects of the action of ozonized air on wool, studied by S. R. Trotman and D. A. Langsdale,³⁹ indicate that the properties of wool damaged by ozone are very similar to those of over-chlorinated wool. Perhydrol (30% hydrogen peroxide) rapidly attacks and dissolves wool to a clear solution. P. Waentig⁴⁰ finds that wool is practically unaffected by sunlight or by light from the mercury vapour lamp.

SILK.

But little scientific work on silk is to be noted during the past year. The action of light on the fibre has been studied by P. Waentig,⁴¹ who finds it only slightly more sensitive than wool, and R. O. Herzog,⁴² as the result of Röntgen-ray examination, states that silk, like cotton and other textiles, is built up of minute crystals, one axis of which runs parallel to that of the fibre.

A scheme for the analysis of raw silk is given by F. Utz.⁴³

FLAX.

A useful research of G. Ruschmami⁴⁴ introduces a new method of staining whereby the micro-organisms on scutched flax can be revealed and their number and position examined. The number on retted flax is high. After 14 days' incubation the moistened flax lost 25% of its strength. The attack was due to spore-forming bacteria, the number of aerobic forms greatly preponderating. The bacteria attack chiefly the pectin, loosening the bonds between the fibres, but in part also the cellulose itself. The author states that the permissible moisture in flax, 12.5%, is too high, considering that the figure for cotton is only 8.5%.

W. Kind⁴⁵ has examined the differences in bleaching that were to be found among yarns spun from flax which had been retted to different stages. After close examination of under- and over-retted flax, the conclusion is reached that to the bleacher the degree of retting makes no difference, but that it is of some significance to the spinner.

³⁸ *Textilber.*, 1923, **4**, 237.

³⁹ *J.*, 1923, 13T.

⁴⁰ *Z. angew. Chem.*, 1923, **36**, 357; *J.*, 1923, 825A.

⁴¹ *Ibid.*,

⁴² *Chem.-Zeit.*, 1923, **47**, 21.

⁴³ *Ibid.*, 1923, **47**, 36; *J.*, 1923, 177A.

⁴⁴ *Faserforsch.*, 1923, **3**, 131.

⁴⁵ *Textilber.*, 1923, **4**, 22.

The decortication of flax under pressure generally leads to a weakening of the strength of the fibre, owing to the acids produced decomposing the pectin in the fibre bundles, with consequent loss of tenacity. G. Ruschmann⁴⁶ overcomes this by a preliminary leaching, and claims that the fibre is then not damaged by several treatments at four atmospheres pressure.

A process for the "cottonising" of flax-waste has been worked out by P. P. Budnikoff and P. W. Solotareff.⁴⁷ The waste is heated under pressure with alkali and sodium bisulphite, and the treatment repeated with liquors of diminishing concentration. The loss in weight produced is of the order of 30%.

BAST AND OTHER VEGETABLE FIBRES.

A valuable study of the behaviour of bast fibres under the influence of caustic alkalis is contributed by C. R. Nodder and R. W. Kinkead,⁴⁸ of the Linen Industry Research Association. It must be read in conjunction with the authors' previous work⁴⁹ in which they showed that the component fibrils of flax and ramie fibres are arranged in left-handed spirals. The contraction produced by caustic soda solutions of various degrees of concentration on fibres of ramie and of flax has been measured. With ramie there is a remarkably sharply defined contraction maximum with a 10% solution of sodium hydroxide (22.2° Tw.). Flax shows a somewhat similar series of curves. The untwisting of ramie was carefully examined, and the results show that the maximum untwisting takes place with solutions producing the greatest contraction. The work includes a study of yarns, a comparison of bast fibres with cotton, and a discussion of the effects observed in relation to lustre in mercerised goods. An interesting account of the spinning, mercerising, and dyeing of ramie was recently given by W. Marshall.⁵⁰

The possibilities of the recently introduced Arghan fibre are discussed by G. A. Lowry⁵¹ and by A. Montefiore.⁵² The cleaning of the fibre on a commercial scale is very difficult. It is stated that a machine has now been invented for doing this which should pave the way to the use of Arghan as a textile fibre. There is little doubt that for cordage purposes Arghan has a future, especially as its resistance to sea-water, determined by the present writer, is very high. There appear, however, to be many difficulties connected with the fibre from the spinning point of view.

⁴⁶ *Faserstoffe*, 1923, **5**, 50.

⁴⁷ *Z. angew. Chem.*, 1923, **36**, 138; cf. *Abs.*, 1924, B, 11.

⁴⁸ *J. Text. Inst.*, 1923, **14**, 133T.

⁴⁹ *Ibid.*, 1922, **13**, 161.

⁵⁰ *J. Soc. Dyers and Col.*, 1922, **38**, 293.

⁵¹ *J. Roy. Soc. Arts*, 1923, **71**, 137.

⁵² *J. Text. Inst.*, 1923, **14**, 20P.

A useful summary of the botany, structure, etc. of Arghan is given by G. van Iterson.⁵³

C. Sunder⁵⁴ describes methods for the preparation of nettle fibres. The difficulties are numerous, since the air-dry stalks contain only 6% of fibre, with 85% of ligneous substances and 9% of incrusting matter. The fibres are, however, more lustrous than cotton and easily dyed.

Since 1919 English importers of Abaca have constantly had to complain of the occurrence, especially among the lower grades of Manila hemp, of a large proportion of weak, brittle, and discoloured fibre. The trouble was early diagnosed as due to micro-organisms, but attempts to produce the effects on sound high-grade hemp did not succeed. The Department of Agriculture and Natural Resources of the Government of the Philippine Islands⁵⁵ has lately succeeded in isolating from damaged fibre a number of species of micro-organisms, including one sterile fungus and four species of bacteria. These were severally inoculated on to sound fibre of grades A and J. It was found that those capable of producing the damage on grade J included the sterile fungi, *A. niger* and another *Aspergillus* species. Only a trace of damage was found on grade A after one month. The conclusion is reached that the causal organisms live mainly on the starch content of the pulp present in the coarser grades of fibre. It is believed that the damage can be minimised or removed by (a) proper drying before depositing in the warehouse, (b) adequate ventilation of the warehouse, (c) avoiding too long storage and, if the market permits, stopping the production of grades J to M.

ARTIFICIAL SILK.

Although the world's production of artificial silk for 1922 exceeded 36 million kg. (*Bulletin des Soies et des Soieries*, Lyons), yet this was insufficient to supply the demand. In consequence, new works are being set up and constant research work is doubtless in progress, though not very much of it is available in published form. The United States output of 10 million kg. in 1922 compares with $2\frac{1}{2}$ million kg. in 1918. In Germany at the beginning of 1923 the output had reached as much as 600 metric tons per month. According to the report of the Société de la Soie de Tubize considerable developments are taking place in the manufacture of acetate silk, and the National Resources Bureau of the Department of the Interior of Canada has prepared a memorandum dealing with the possibility of establishing the artificial silk industry, probably in the form of acetate silk, in that country.

⁵³ *Med. Rijksraad. Vezelhandel, Delft*, 1923, **8**, 73.

⁵⁴ *Bull. Soc. Ind. Mulhouse*, 1923, **89**, 187; *J.*, 1923, 649A.

⁵⁵ *D.*

On the technical side numerous patents are in evidence relating to improvements in the production of very fine threads of viscose silk. *Glanzfäden A.-G.*⁵⁶ protect the addition of per-acids and their salts to the spinning bath for the elimination of minute bubbles of hydrogen sulphide formed during the coagulation of fine threads. E. Brommert⁵⁷ finds that threads of 1-6 deniers made according to his previous patent⁵⁸ lack softness and tend to stick together. These defects are overcome by adding to the spinning bath a mixture or solution prepared by treating a mixture of cellulose and concentrated sulphite waste-liquors with 80% sulphuric acid.

Satisfactory viscose threads, films, and ribbons are prepared by A. Kämpf⁵⁹ by using in the spinning bath a solution in sulphuric acid of the condensation product obtained by the treatment of wood with phenol.⁶⁰

Improvement in the resistance of viscose silk to the action of water has long been desired. H. Delahaye⁶¹ claims to produce a silk practically unaffected by water by preparing the alkali cellulose at 0° C., keeping it at this temperature for several days, and then at 15° for several days to allow of a slight hydration; converting into the xanthate at temperatures below 20°, and finally preserving the product for one to three weeks at below 10°.

The production of a readily soluble viscose using less caustic soda and carbon bisulphide than is generally employed, is described by Technochemia A.-G.⁶² who attain this result by boiling the cellulose for 6 hours with 0.5% sulphuric acid before treatment with the mercerising soda at 5° C. The xanthate can be used at once or stored at 5° till needed.

The Snia Societa⁶³ finds that the organic by-products formed in the spinning bath have a beneficial effect on the finished silk, and recommends that the exhausted liquors be concentrated, acidified, and added to the next spinning bath.

Published developments in connexion with cellulose acetate silk relate chiefly to dyeing and finishing.

YARNS AND FABRICS.

Testing.

A scheme outlined by the Cotton Research Co. of Boston, U.S.A., includes a complete unit of standard mill machinery, coupled with laboratories in which standard testing and research can be

⁵⁶ E.P. 185,718; *J.*, 1923, 446A.

⁵⁷ E.P. 192,214; *J.*, 1923, 305A.

⁵⁸ E.P. 166,931; *J.*, 1921, 654A.

⁵⁹ E.P. 184,450; *J.*, 1923, 711A.

⁶⁰ E.P. 160,482; *J.*, 1921, 344A.

⁶¹ E.P. 195,569; *J.*, 1923, 494A.

⁶² E.P. 193,920; *J.*, 1923, 493A.

⁶³ E.P. 178,121; *J.*, 1923, 883A.

conducted. The question of the mechanical testing of yarns and other cotton materials has been considered in a comprehensive report from the British Cotton Industry Research Association.⁶⁴ The report begins with a very much needed discussion on terminology and the principles on which methods are based, and goes on to define these in precise physical terms. The interpretation of data by the aid of statistical methods is considered. A full treatment of the various machines from the point of view of their working principles is contributed by E. Midgley, and a summary of past work relating to the effect of humidity and temperature conditions on the results obtained in testing is furnished by A. R. Urquhart. His conclusions are that only a general idea of the effect of humidity on strength can be obtained from previous results; that results must be treated statistically on the basis of a very large number of tests. Work on these lines is foreshadowed by A. J. Turner.⁶⁵

A review of this subject of yarn testing, with special reference to linen yarns, is contributed by T. Hemmerling,⁶⁶ who deals theoretically with the questions of statistics and their application, the clinging power, breaking length, etc. A spring dynamometer, which automatically records the load-extension curve, and a simple machine for the testing of oscillating stress, are described. The papers constitute a thoughtful, if not final, account of testing principles and should be read.

Recent experiments with the Jumbo Mullen Tester⁶⁷ have made it possible to express the strength of materials tested by it in terms of an Index Value. This figure is obtained by dividing the bursting strength of the fabric by the weight of unit area. As both warp and weft strengths are included in this single figure, it is claimed that the Index Value will prove to be a most useful test, especially for quality in fabrics of the same construction, but made from different grades of cotton.

A. E. Owen and A. E. Oxley⁶⁸ have continued their studies on the physical properties of yarns under oscillating stresses. A method is described whereby the regularity of a yarn is measured by its capacity to withstand an oscillating tension which never approaches the breaking strength. Such tensions are similar to those produced in weaving, and it is found that a yarn which could stand indefinitely a load equal to the maximum of such tensions gives way in time to such a series of impulses. The extension of yarns under these conditions has been recorded and expressed in terms

⁶⁴ *J. Text. Inst.*, 1923, **14**, 161-208T.

⁶⁵ *Ibid.*, 1923, 45T.

⁶⁶ *Textilber.*, 1923, **4**, 5, 63, *et seq.*

⁶⁷ *J. Text. Inst.*, 1923, **14**, 329T; *Text. World*, 1923, **64**, 117.

⁶⁸ *Ibid.*, 1923, **14**, 18T.

of accumulated permanent slip of the hairs. The method should prove exceedingly useful, since it tends to exaggerate and reveal small differences in yarns due to faults in the spinning, weaving and sizing processes.

A. E. Owen⁶⁹ has, in a later paper, described the behaviour of sized yarns under the oscillating stress tester. As would be expected, sizing increased the resistance of the yarn to repeated variation in tension, such as might occur in weaving. It is interesting to note that various sizing mixtures examined gave almost identical improvement in resistance, and this is explained by the assumption that in all these mixtures the cementing action of the size on the fibres is complete. Sizing entails a reduction in the ultimate extension-value, and the author suggests the possibility of a size which, while retaining the cementing action, might permit of a greater longitudinal movement of the fibres.

CELLULOSE.

Physical and Colloidal Properties.

It is by accurately compiled knowledge of the physical state of cellulose and its esters in various stages of colloidal dispersion that we may hope to advance, not only in knowledge of the molecular structure and condition of these derivatives, but also in the perfection of their applications in technology.

A series of studies by E. W. J. Mardles,⁷⁰ in which a vast amount of experimental observation is recorded, point the way to a clearer understanding of many points in the science and technology of cellulose esters. In a research on suitable pure and mixed solvents for the acetate, chloroacetate, and nitroacetate, the author finds that the solubility of an ester or, otherwise regarded, the dispersing action of a liquid, depends on the relative specific character of the liquid and the ester respectively. If the lower members of a homologous series, e.g., benzyl and tolyl alcohols, are good solvents there is invariably a rapid fall in activity as the series is ascended, and from this regularity the conclusion is drawn that liquids with smaller molecules, and consequently larger "residual affinity," are the better dispersing media. For example, aniline has solvent properties, but dimethylaniline is a non-solvent. A mixture of liquids by no means possesses a solvent power of an average value between the constituents. Some non-solvents become solvents when suitably mixed, while in some cases solvents become non-solvents. There does not appear to be any relation between the solvent power of a liquid and its dielectric constant, molecular refractivity, or molecular volume.

⁶⁹ *Ibid.*, 1923, **14**, 375T.

⁷⁰ *J.*, 1923, 135T, 209T; *Trans. Faraday Soc.*, 1923, **18**; *J.*, 1923, 178A.

The author finds also that the volume change accompanying the formation of cellulose ester organosols is greatest with the best solvents (or optimum mixture in the case of mixed solvents), and that it increases with temperature and with dilution.

Approaching next the question of gel formation, Mardles⁷¹ has examined the viscosity changes with time (*a*) during gelation, and (*b*) during gel-to-sol transition in the case of cellulose acetate solutions in benzyl alcohol. The falling-sphere viscosimeter was used, but as gelation proceeded the balls fell irregularly, so that only approximate measurements could be made. By producing the viscosity-time curves the temperature at which the rate of gelation was zero could be obtained. This maximum gelation temperature is one above which the sol would be comparatively stable and below which gel formation would begin. This temperature increases rapidly with the concentration.

Assuming that the scattering of light by a colloid mixture is intimately connected with the size of the particles present, measurements were made of the "Tyndall number" of organosols and gels of cellulose acetate. A sol cooled without agitation shows a small increase in the Tyndall number until the maximum gelation temperature is attained; thereafter during gelation increase is rapid, but it falls off quickly after the formation of a definite jelly. The Tyndall number increases rapidly with concentration up to a definite concentration, notably 6 g. of cellulose acetate per 100 c.c. of benzyl alcohol. A connexion between this Tyndall number and the volume change is to be noticed, since both are most pronounced at this particular concentration.

Studies of the elasticity of organogels of cellulose acetate, also by Mardles,⁷² showed that this quality varies enormously with age, preparation, etc. of the gel, and the measurements obtained prove difficult to adapt to any very definite relationship.

These results may be considered as promising indications of advance in this field. They go to show that the order of formation of a gel is probably, first the aggregation of the dispersed ester-colloid into larger units, then the coupling of these units into groups, and finally the linkage of the groups into the gel.

J. Duclaux⁷³ develops a theory of the constitution of reversible gels such as those of cellulose nitrate. According to this the gel consists of an insoluble solid resembling the cellules of a sponge and of a soluble solid which can be either colloid or crystalloid. The former is associated with the solvent as an irreversible gel, while the latter is in solution in the solvent. The mechanical

⁷¹ Faraday Soc., *loc. cit.*

⁷² *Ibid.*, April, 1923; *J.*, 1923, 649A.

⁷³ *Bull. Soc. Chim.*, 1923, 33, 36; *J.*, 1923, 293A.

properties of the gel are dependent upon the ratio of the insoluble to the soluble solid. In a solution of nitrocellulose prepared cold the insoluble solid is present in large proportion, and this is evident in the high viscosity and tendency to gelation of such a solution as compared with one prepared at a higher temperature.

The viscosity of a specially prepared nitrocellulose solution has been measured by I. N. Kugelmass⁷⁴ between -90° and +35° C. He finds that in this and its other physical properties the ethereal solution of nitrocellulose resembles an ordinary colloidal solution in water.

R. A. Joyner⁷⁵ has continued his studies on the lowering of the viscosity of cellulose by acids, sodium hydroxide, and air. A mass of experimental results is given in this interesting paper, but the author himself points out the difficulties of their interpretation. He finds that the highest viscosity possible for a 2% solution of cellulose is 57,000 seconds (or 28,000 abs. units), while by repeated kiering of a cellulose with sodium hydroxide a viscosity of 1 second for a 5% solution was obtained, which is regarded as the minimum. The hypothesis is put forward that there are two kinds of cellulose : cellulose A with the higher viscosity and cellulose B with the lower. From the measurements with air it was calculated that the amount of oxygen necessary to convert cellulose A into cellulose B was 16 grams per 2100 grams of cellulose. With hypochlorite oxygen the proportions were similar, viz., 16 of oxygen to 2500 of cellulose. These results are very important and should throw a light on the complex physico-chemical balance of cellulose. They must be considered carefully by the pure chemist, who is apt to regard cellulose as a rigid chemical unit. He must help, for example, in explaining the remarkable fact that a brief exposure of a cuprammonium solution of cellulose to air and light produces enormous changes in its viscosity.

A report on the viscosity of such solutions is issued by the Research Department, Woolwich,⁷⁶ in which all necessary precautions to be taken in purifying and sampling the cellulose, preparing the solutions, filling and using the viscosimeters are given. An exact specification for making the cuprammonium solution is included.

A new viscosimeter specially suitable for colloidal solutions is described by P. Secomte du Noüy,⁷⁷ which does away with the capillary tube and yet requires no more than 1 c.c. of fluid. The principle is that of co-axial cylinders.

⁷⁴ *Rec. Trav. Chim.*, 1922, 41, 751; *J.*, 1923, 246A.

⁷⁵ *Chem. Soc. Trans.*, 1922, 121, 2395; *J.*, 1923, 90A.

⁷⁶ Report No. 22; *J.*, 1923, 970A.

⁷⁷ *J. Gen. Physiol.*, 1923, 5, 429.

Chemistry and Constitution.

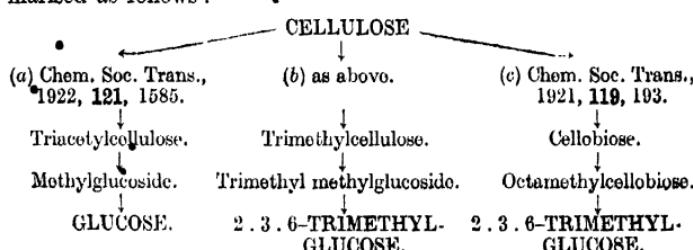
The question important to all workers on the chemistry of cellulose of the preparation of a standard cotton cellulose has been investigated by a Committee of the Division of Cellulose Chemistry of the American Chemical Society.⁷⁸ Starting with Wannamaker's Cleveland raw cotton, elaborate instructions are given for boiling off and bleaching. The purity is controlled by selected methods of analysis which have been investigated. The cellulose content obtained varied between 98·4 and 99·6%, the general standard of purity resembling that of the Madder bleach calico recommended by Cross and Bevan.

A ready method of obtaining cellulose free from lignin and pentosan is given by C. G. Schwalbe (see p. 153).

The outstanding contribution of the year in the field of cellulose chemistry is the work of J. C. Irvine and E. L. Hirst⁷⁹ on the molecular structure of cotton cellulose. The results now obtained by them enable a formula to be given for the cellulose unit complex, an achievement which crowns a series of exact investigations pursued over a long period of years. The experimental work described consists in (1) the preparation of the fibrous trimethylcellulose $C_6H_7O_2(OMe)_3$, and (2) the simultaneous hydrolysis of this substance to a methylated glucose and condensation of this with methyl alcohol by the action of a methyl alcoholic solution of hydrogen chloride.

The second process, theoretically considered, can proceed in many ways and might result in the formation of one, four, twenty and even up to forty-nine methylated sugars. By a remarkable chance experiment showed that methylated cellulose broke down in the simplest of all these ways : only one sugar, 2.3.6-trimethylglucose, was obtained.

Before discussing the bearing of these results the three main degradation series initiated by Irvine and his co-workers are summarised as follows :—*

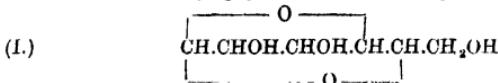


* The reader will find a summary of previous work on the constitution of cellobiose, trimethylglucose, etc., in "Researches on Cellulose," Vol. IV., by C. F. Cross and C. Doré. (Longmans, Green and Co., 1922.)

⁷⁸ *Ind. Eng. Chem.*, 1923, 15, 711; *J.*, 1923, 825A.

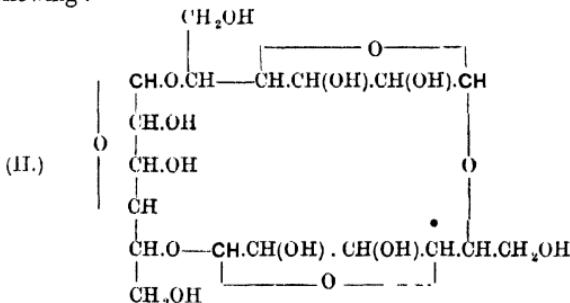
⁷⁹ *Chem. Soc. Trans.*, 1923, 123, 518; *J.*, 1923, 710A.

The simplest cellulose molecule which will satisfy series (a) and (b) is a 1,5-anhydroglucose of the butylene-oxide type (I).



This structure, however, could not yield cellobiose in accordance with the results of series (.), and the simplest structure which would conform to this requirement would be a di-anhydroglucose of the same unit structure. If, however, cellulose were constituted in this way 100 parts would be capable of producing 105.5 parts of cellobiose.

Whilst it is well known that 35 parts is the yield more commonly obtained, and making all allowances, the authors consider that a grouping which would allow of 50 to 70% of cellobiose would be the safest hypothesis in the light of present knowledge. They therefore give a number of tri-anhydroglucose formulæ which, while satisfying all other conditions, involve a maximum yield of cellobiose of 70%. Of these they express preference for the following :—



(Letters in block type indicate potential reducing groups.)

In a further discussion the authors demonstrate the failure of all the older formulæ in the light of one or other of these results.

A point in connexion with formula II. (which permits of cellobiose as the only disaccharide obtainable on hydrolysis) is raised by the isolation of a new trisaccharide of dextrose from the products of the acetolysis of cellulose. G. Bertrand and S. Benoist⁸⁰ give details of the method by which they isolated the new sugar, m.p. 210°C., $\alpha_D = +22.8^\circ$, to which they have given the name procellose. They are also able to show that the so-called iso-cellobiose of Ost and Prosiegel⁸¹ is a mixture of procellose with cellobiose.

The formation of ω -bromomethylfurfural from ketoses and cellulose, but not from dextrose and other aldehydic sugars, has hitherto been accepted, and on this fact many writers have postulated

⁸⁰ *Comptes rend.*, 1923, 176, 1583; *J.*, 1923, 848A.

⁸¹ *J.*, 1920, 421A.

the existence of a ketonic grouping in the cellulose molecule. H. Hibbert and H. S. Hill⁸² now find that dextrose and derived sugars can be made to give 3 to 12% of ω -bromomethylfurfural, and that therefore there is no experimental justification for the assumption of a ketonic character for cellulose.

It is true that this may be held to support the constitution assigned to cellulose by Irvine, but the very simplicity of this formula prevents it from explaining some quite definite reactions of cellulose. Thus J. Hübner and J. N. Sinha⁸³ find that iodoform can always be obtained in minute quantities by the action of iodine on cellulose followed by dilute alkali, the iodoform being produced from some volatile product liberated by the alkali. This is one of several other cases in which small quantities of product are obtainable from the cellulose complex, and their formation certainly requires explanation.

The constitution and structure of cellulose are considered in another way by K. Hess,⁸⁴ who concludes that in cuprammonium solution cellulose may exist as $C_6H_{10}O_5$ units. X-ray examination of cellulose fibre and cellulose precipitated from the solution shows that the chemical structure is not apparently altered. The varying solubility, e.g., in alkali, of cellulose products having the same chemical structure, is explained as being due to the degree of packing of the units, a loose arrangement permitting of greater solubility than a closely packed one in which the more basic groups are masked. If cellulose is $C_6H_{10}O_5$, cellobiose must be built up from separate cellulose molecules, and on this hypothesis the author explains that, on the hydrolysis of cellulose, the yield of cellobiose, owing to alternative reactions, is not more than 33%.

L. E. Wise⁸⁵ discusses the relationship of cotton cellulose to the cellulose of the woods. He considers that the balance of evidence is in favour of a large aggregate for the cellulose complex, the aggregate being made up of comparatively small cellulose units: each unit again containing the anhydro-cellobiose linkage relatively few times. On this hypothesis the complex is likened to a brick wall, the cellulose units being the bricks held together by a mortar of secondary valencies.

The author considers wood cellulose to be a complex of a more variable character, the greater number of the units being identical with those of the cotton cellulose complex, together with a few consisting of carbohydrates adsorbed during cell growth.

The extent to which the cellobiose linkage occurs in the cellulose derived from a number of American woods—red spruce, white

⁸² *J. Amer. Chem. Soc.*, 1923, **46**, 176; *J.*, 1923, 219A.

⁸³ *J.*, 1923, 255T.

⁸⁴ *Z. angew. Chem.*, 1923, **36**, 502.

⁸⁵ *Ind. Eng. Chem.*, 1923, **15**, 711; *J.*, 1923, 825A.

oak, etc.—has been examined by L. E. Wise and W. C. Russell,⁸⁶ who investigated the α -celluloses obtained. By very careful acetolysis cellobiose octa-acetate was isolated, the yields varying from 24 to 33% of the theoretical compared with 33% from cotton cellulose. They consider that the cellobiose linking must occur in wood cellulose to the extent of 24%, or possibly as much as 50%.

A review of these results would seem to show that the most resistant portion of the cellulose of woods is very similar to, if not identical with, cotton cellulose, but that the wood cellulose complex taken as a whole is different from cotton cellulose in that it contains other and less stable groupings.

The mechanism of the acetolysis of cellulose by acetyl bromide has been studied by L. Zechmeister,⁸⁷ and on the synthetic side H. Hibbert and H. S. Hill⁸⁸ have initiated some promising investigations on the condensation reactions of *p*-bromoacetaldehyde whereby hydroxy-derivatives, closely related to the polysaccharides and anhydro-sugars, have been prepared.

Cellulose Degradation Products.

A useful summary of the literature relating to hydrocellulose is given by P. H. Clifford.⁸⁹ E. Heuser and F. Eisenring,⁹⁰ in continuation of their work on hydrocellulose, have examined the action of oxalic acid solutions of 8 to 16% concentration at 100° and 180° C. on cellulose from viscose. By such treatments hydrocellulose products having a copper number of 10 or more, and completely soluble in 8% sodium hydroxide are obtained.

Viscose hydrocellulose, if heated for 30 minutes at 180° with oxalic acid, gave nearly 12% of ω -hydroxymethylfurfural, while viscose cellulose gave 5.7%, and cotton cellulose only 0.8%.

These and other peculiarities shown by viscose cellulose obviously require further work for their elucidation.

But little work is reported on oxycellulose. E. Knecht and J. P. Egan⁹¹ find that an oxycellulose with, for example, a copper number of 15, is produced by hypochlorous acid with about one-tenth of the oxygen required when the oxidation is brought about by acidified permanganate solution. The development of colour noticed by A. E. Everest and A. J. Hall, which is produced when a highly oxidised cellulose is treated with tetrazotised benzidine solution, has been further examined by the authors.⁹² The reducing property is lost after extraction of the oxycellulose with alkalis.

⁸⁶ *Ind. Eng. Chem.*, 1923, **15**, 815; *J.*, 1923, 923A.

⁸⁷ *Ber.*, 1923, **56**, 573; *J.*, 1923, 347A.

⁸⁸ *J. Amer. Chem. Soc.*, 1923, **45**, 734; *J.*, 1923, 347A.

⁸⁹ *J. Text. Inst.*, 1923, **14**, 69T.

⁹⁰ *Cellulosechem.*, 1923, **4**, 25; *J.*, 1923, 649A, 599A.

⁹¹ *J. Soc. Dyers and Col.*, 1923, **39**, 67; *J.*, 1923, 349A.

⁹² *Ibid.*, 1923, **39**, 47; *J.*, 1923, 219A.

Cellulose Esters and Ethers.

Progress in the manufacture of these derivatives continues to lie rather in improvement in the details of the older processes than in the introduction of new principles.

H. Plauson,⁹³ however, prepares pure or mixed cellulose esters by working with very finely divided cellulosic material in the presence of gaseous agents such as the vapours of acetic or formic acids, a gaseous catalyst, such as sulphur dioxide, being employed.

The Eastman Kodak Co.⁹⁴ make a novel claim for the production of cellulose ethers in that the reaction between the alkali-cellulose and the etherifying agent is brought about in the presence of a large surface of "immunised steel." H. Dreyfus⁹⁵ is able to reduce the quantities of alkali and etherifying agent practically to the theoretical value, by reducing the amount of water present, so that the ratio water:cellulose is less than 4 : 1 and preferably 0 to 0.5 : 1. This is accomplished by the addition of water-binding agents, such as the oxides of the metals of the alkaline-earths.

H. Gault and P. Ehrmann⁹⁶ find that hydrocellulose readily yields esters of the higher fatty acids, e.g., a distearic ester, under the action of the acid chloride dissolved in benzene in the presence of pyridine at 110° C.

The production of inorganic esters in fibrous form, giving a material resembling wool in some of its properties and suitable also for the manufacture of very strong paper, is claimed by Burgess, Ledward and Co. and W. Harrison.⁹⁷ Cotton, hemp, jute, or wood is impregnated with caustic soda solutions of 12 to 20% concentration and squeezed to hold its own weight of liquor. The "mercerised" material is then treated for 5 to 15 minutes with thionyl, phosphoryl or other chloride below 40° C. A lustrous finish may be obtained by esterifying under tension.

E. Knoevenagel and K. König⁹⁸ have recorded and discussed the condensation or polymerisation shown by cellulose acetate solutions on standing. J. O. Zdanowich⁹⁹ claims that such solutions can be stabilised by the addition of small amounts of aqueous solutions of aldehydes. Treated in this way the "acetose" solutions on standing show a constant viscosity and give a stronger film or thread.

Patents for the production of plastics containing cellulose esters or ethers continue to appear, the novelty consisting in the addition

⁹³ E.P. 200,160; *J.*, 1923, 883A.

⁹⁴ U.S.P. 1,437,820-1; *J.*, 1923, 91A.

⁹⁵ E.P. 187,639; *J.*, 1923, 10A.

⁹⁶ *Comptes rend.*, 1923, 177, 124; *J.*, 1923, 826A.

⁹⁷ E.P. 192,173; *J.*, 1923, 304A.

⁹⁸ *Cellulosechem.*, 1922, 3, 113; *J.*, 1923, 140A.

⁹⁹ E.P. 200,186; *J.*, 1923, 925A.

of various compounds which at present appear to be determined by the method of trial and error.

The Eastman Kodak Co.¹⁰⁰ for one composition employ phenylpropyl alcohol as a solvent, and in another¹⁰¹ a lower monohydroxy-aliphatic alcohol with the addition, for example, of furfural. Films prepared from a solution of cellulose ether in an aromatic alcohol of the type of benzyl alcohol, together with methyl alcohol, are found to have increased durability and flexibility, while the addition of various nitrogenous compounds such as methylacetanilide gives greater stability and heat resistance.

The addition of ethylenethiohydrin and its esters was protected by Meister, Lucius, u. Brüning¹⁰² for the preparation of very pliable films and artificial leathers, and another series of sulphur compounds, viz., the mixed aromatic and aliphatic sulphones of the formula R.SO₂.R¹, e.g., the amyl sulphone of benzene, was found by Kalle u. Co.¹⁰³ to give additional softness and durability.

Ethyldiene-diphenol is recommended¹⁰⁴ as a substitute for camphor in the production of a clear elastic celluloid, and again acetonitrile is employed¹⁰⁵ as a solvent in the manufacture of celluloid with camphor or its substitutes.

An interesting study of nitrocellulose in relation to the manufacture of celluloid is contributed by K. Atsuki.¹⁰⁶ The minimum percentage of camphor in 95% alcohol, which will bring about complete solubility of the ester, is defined as the "camphor number." The value of this for a normal nitrocellulose containing 11% of N is 8-10, a higher number being required for nitrocelluloses containing more, or less, nitrogen than this. The minimum viscosity of such solutions is obtained with 35% of camphor in the solvent. For the manufacture of nitrocellulose the conditions are, first, solubility, i.e., maximum dispersion, and secondly, minimum viscosity. These conditions are attained by using a nitrocellulose made from a normal cellulose with a camphor number as above, together with 80 to 140 parts of solvent, the latter consisting of 65 parts of 95% alcohol and 35 parts of camphor.

WOOD, STRAW, ETC.

A. C. von Euler¹⁰⁷ offers a useful contribution on the quantitative composition of the coniferous woods. She differentiates the pure

¹⁰⁰ U.S.P. 1,444,331; *J.*, 1923, 305A.

¹⁰¹ U.S.P. 1,450,714-6; *J.*, 1923, 494A.

¹⁰² U.S.P. 1,460,690 and 1,460,097; *J.*, 1923, 925A.

¹⁰³ G.P. 866,115-6; *J.*, 1923, 348A.

¹⁰⁴ G.P. 367,560; *J.*, 1923, 397A.

¹⁰⁵ G.P. 368,476; *J.*, 1923, 600A.

¹⁰⁶ *J. Coll. Eng. Tokyo Imp. Univ.*, 1922, 13, 1; *J.*, 1923, 263A.

¹⁰⁷ *Cellulosechem.*, 1923, 4, 1; *J.*, 1923, 346A.

wood substance from non-constitutional substances, such as fat, resin, proteins, and mineral matter. The wood substance proper she defines as (*a*) cell wall carbohydrates, (*b*) incrusting and interpenetrating substances, chiefly lignin, (*c*) soluble tannins, colouring matters (usually of the flavone type), both related to lignin. Criticising existing methods of analysis, the author gives reasons for regarding the "alcohol-resin" as a soluble variety of lignin. In spite of previous recommendations she considers that insoluble lignin may be determined either by means of 40% hydrochloric acid or by 72% sulphuric acid, the results in the latter case being about 5.7% higher owing to combination of the lignin with SO_4H groupings. With both methods the acetyl grouping, which constitutes about 2% of the wood, is removed and the lignin values must be corrected accordingly.

G. J. Ritter and L. C. Fleck¹⁰⁸ publish analyses of a large number of American woods, some not previously examined. On acid hydrolysis, hard woods yield a larger proportion of acetic acid than soft woods, and contain twice as much pentosan constituent on the average. The celluloses isolated from the soft woods retain 38–56% of the furfural-yielding groups contained in the wood, while the cellulose from the hard woods retains 60–66%.

A study of the products obtained on the hydrolysis of white spruce wood by dilute sulphuric acid under steam pressure, carried out by E. C. Sherrard and G. W. Blanco,¹⁰⁹ showed that as much as 24% of sugars could be obtained under the working conditions. These were identified, and their relative proportions determined, by fermentation methods, mannose being the chief constituent (38%), followed by dextrose (29%), xylose (13%), galactose (6%), arabinose (5%), in order. White spruce on hydrolysis gave dextrose and mannose in the ratio 3 : 1, while cotton cellulose gave only dextrose, the pentose sugars being absent. These facts are discussed in connexion with the nature of wood cellulose. The addition of small quantities of metallic salts, especially mercuric chloride, was found by the same authors¹¹⁰ to increase the amount of fermentable sugars obtained in the hydrolysis of spruce wood, while a preliminary treatment of the wood with caustic soda diminished the yield and chlorination, followed by sodium sulphate solution, inhibited it.

Contributions to the analytical determination of cellulose in wood include R. Sieber's suggestion¹¹¹ that chlorine water can be employed instead of chlorine, thereby ensuring greater penetration of the wood and less risk of attack on the cellulose. The process is carried out in an open cylinder, covered at one end by a calico filter.

¹⁰⁸ *J. Ind. Eng. Chem.*, 1922, **14**, 1050.

¹⁰⁹ *Ind. Eng. Chem.*, 1923, **15**, 611; *J.*, 1923, 710A.

¹¹⁰ *Ibid.*, 1923, **15**, 63; *J.*, 1923, 286A.

¹¹¹ *Zellstoff u. Papier*, 1923, **3**, 27; *J.*, 1923, 492A.

L. Kaib and V. Schoeller¹¹² and also E. Legeler¹¹³ describe the use of phenol for cellulose determination. Phenol reacts with lignin, forming, apparently, a condensation product of a resinous character which dissolves in excess of phenol. A small amount of mineral acid is, however, essential for a rapid and quantitative conversion. Suitable conditions for working are : wood 4 parts, phenol 50, hydrochloric acid 0·05, heating for 1 hour on the water bath. The results are concordant, but lower than those given by the chlorination method.

C. G. Schwalbe¹¹⁴ states that up to now there has been no simple method of obtaining a (wood) cellulose free from lignin and pentosans. He finds, however, that heating with magnesium sulphite solutions in the presence of lime or magnesia effects the complete removal of these substances.

A volumetric method for determining the proportions of α -, β -, and γ -cellulose in a cellulosic material is described by M. W. Bray and T. M. Andrews.¹¹⁵ The authors state that a solution of cellulose in 72% sulphuric acid is oxidised by potassium bichromate. The bichromate solution is standardised against 1 gram of pure cellulose, the α -precipitate dissolved, and estimated against this standard; the β is precipitated and removed, and the γ determined also with bichromate, the quantity of β being found by difference. It is claimed to be a quicker and more accurate process than the gravimetric one, and deserves a trial.

LIGNIN.

A great deal of attention has been devoted to the chief non-cellulosic constituent of woody fibres, lignin or lignone. This substance can be obtained (a) by the action of alkalis—a method of extraction, (b) by the action of highly concentrated hydrochloric acid (Willstätter), which hydrolyses the cellulose to soluble products, and (c) as a sulphonate acid by the action of bisulphites. In each case, however, it suffers more or less change in the process of isolation.

E. Beckmann, O. Liesche, and F. Lehmann¹¹⁶ have made an exact study of the first method, examining the lignins from various straws and woods. The action of the 1·5% sodium hydroxide was examined under conditions of increasing severity as to temperature and pressure. With the straws, the methoxyl content reached its highest value in lignins isolated by boiling for 6 hours under a reflux: with woods, 6 hours at 90 lb. pressure was needed to give a product of maximum methoxyl content. With increasing temperature all the products became darker and less readily soluble in selected solvents. On demethylation with hydriodic acid, a straw

¹¹² *Cellulosechem.*, 1923, 4, 37; *J.*, 1923, 881A.

¹¹³ *Ibid.*, 61; *J.*, 1923, 882A.

¹¹⁴ G.P. 378,260; *J.*, 1923, 1017A.

¹¹⁵ *Ind. Eng. Chem.*, 1923, 15, 377; *J.*, 1923, 545A.

¹¹⁶ *Biochem. Zeits.*, 1923, 189, 491; *J.*, 1923, 970A.

lignin gave a compound $C_{36}H_{38}O_6I$, while pine wood lignin gave the more complex substance $C_{108}H_{98}O_{18}I$.

F. Paschke¹¹⁷ finds that straw lignin condenses with aniline to give a product containing three molecules of aniline to one of lignin, and adduces other evidence for the "trivalent" character of lignin, pointing to the presence of three carbonyl groupings. The aldehydic character of straw lignin is further supported by the fact that in dilute alkaline solution it has a genuine tanning action quite unlike that of sulphite liquor.

C. F. Cross and A. Engelstad¹¹⁸ in this connexion claim to prepare a lignone-containing liquor which has a definite tanning action by treating waste wood with six times its weight of 7% sulphurous acid under pressure, neutralising, and concentrating the liquor in a vacuum.

The lignin isolated with the aid of highly concentrated hydrochloric acid continues to be actively investigated. E. Heuser and A. Winsvold¹¹⁹ have examined the products obtained by fusion with potassium hydroxide. Below 240° C. lignic acid is the chief product, but at 280° this is largely decomposed into phenolic substances. Oxalic acid is shown to be a by-product, since if the heating is carried out in an inert atmosphere the amount of it formed falls to zero while that of the phenols correspondingly increases. Proto-catechuic acid is the primary phenolic product, the catechol present in the melt being derived from it by loss of carbon dioxide. The metals, iron, nickel, etc., have an important influence in varying these secondary decompositions.

F. Fischer, H. Schrader, and co-workers in a series of communications only recently available,¹²⁰ have studied the oxidation of lignin and of cellulose with water and dilute alkalis under fairly high pressures. From lignin with 40 hours' treatment mellitic acid, benzenepentacarboxylic acid, and oxalic acid were obtained. Under different conditions benzoic, humic, and isophthalic acids were isolated.

It is known that the lignin isolated by 45% hydrochloric acid readily yields furfural. E. Hägglund¹²¹ shows that a carbohydrate is present and identifies it as arabinose, present to the extent of about 4.5% of the lignin. He regards it as an integral part of the lignin complex, from which it can be removed by digestion with cold concentrated acid. The methoxyl content of lignin freed from carbohydrate is 15.2%.

K. Kürschner¹²² comes to similar conclusions. Lignin, after

¹¹⁷ *Celluloschem.*, 1923, 4, 31; *J.*, 1923, 650A.

¹¹⁸ E.P. 202,016; *J.*, 1923, 971A.

¹¹⁹ *Celluloschem.*, 1923, 4, 49, 62; *J.*, 1923, 492A, 883A.

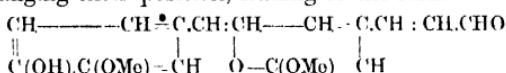
¹²⁰ *Ges. Abhandl. Kennt. Kohle*, 1921, 5, 221, 311, 332; *J.*, 1923, 140A.

¹²¹ *Naturprodukte*, 1923, 24, 35; *J.*, 1923, 970A.

¹²² *Ibid.*, 36; *J.*, 1923, 970A.

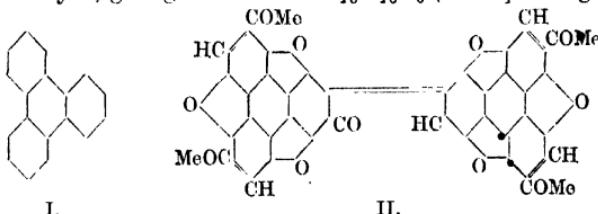
prolonged treatment with concentrated hydrochloric acid, contains no free pentosans. On hydrolysis, however, furfural slowly appears, indicating that a xylan is part of the complex. Xylose was detected both in sulphite cellulose liquors and in lignic acid from the soda process.

Continuing his researches on the constitution of pine lignin, P. Klason¹²³ gives the revised formula $C_{19}H_{18}O_7$ instead of $C_{19}H_{18}O_9$ previously given for the β -lignin isolated as sulphonate acid from bisulphite liquors. The α -lignin he regards as formed by the condensation of two molecules of coniferyl alcohol, two hydrogen atoms changing their position, leading to the formula



A study of the comparative distillation in a vacuum of cellulose, lignin, and resin-free wood carried out by F. Fischer and H. Tropsch¹²⁴ proves that lignin gives no *l*-glucosan. The distillates from wood are more acidic than those from cellulose or lignin. These observations are claimed to indicate that lignin during preparation probably suffers hydrolysis of its acetyl groups and that there is no structural similarity between cellulose and lignin.

The whole of this more recent and previous work is admirably collated by W. Schrauth,¹²⁵ who develops a constitution for lignin which, giving as it does full weight to all the various observations recorded, should be employed by workers on this subject as a basis of criticism and research. Recalling the experiments made by Willstätter and Kalb¹²⁶ on the exhaustive reduction of lignin by means of hydrogen iodide, he demonstrates the great similarity between a hydrocarbon $C_{18}H_{30}$ isolated by them, and a synthetic hydrocarbon prepared by himself of formula I., corresponding to a completely saturated hydrogenation product of 9,10-benzophenanthrene. Schrauth considers that such a structure could arise in the plant by the condensation of 3 molecules of 5-hydroxymethyl-furfuraldehyde, giving a derivative $C_{18}H_{18}O_6$ (corresponding to the



half of formula II. above). Such formulæ contain $\text{CO}\cdot\text{CH}_2$ groupings,

¹²³ Ber., 1923, 56, 300; J., 1923, 177A.

¹²⁴ Naturprodukte, 1923, 8; J., 1923, 966A.

¹²⁵ Z. angew. Chem., 1923, 36, 149.

¹²⁶ Ber., 1922, 55, 2637; J., 1922, 893A.

and if it be assumed that the four such groupings in formula II, are methylated in the enolic form and the elements of hydrochloric acid added at the double linking, we obtain a substance of formula $C_{40}H_{43}O_{11}Cl$ identical with one isolated by Fischer and Schrader from wood substance and containing 13.3% of methoxyl. The agreement between such a formula and the compounds isolated from the calcium bisulphite liquors by Klason and others is also demonstrated.

Investigations at present in progress lead the present writer to give support to such a ring system formula for lignin. He would point out a possible resemblance between lignin and cholesterol and phytosterol, which are known to contain several hydrated rings and in consequence resist all but the most powerful oxidising and reducing agents.

WOOD PULP.

Among other possible sources for wood pulp manufacture, talipot palm leaf stalks and elephant grass from Uganda and Nigeria have been examined by the Imperial Institute.¹²⁷ The former is not suitable for white paper, but the latter proves very satisfactory.

Patents have been granted also for the production of cellulose suitable for paper making from potato tops,¹²⁸ reeds,¹²⁹ banana "trash,"¹³⁰ straw and maize stalks.¹³¹ Sugar cane bagasse and rice-straw have been reported upon for the same purpose.¹³² The importance of establishing a pulp and paper industry in Australia has led to a comprehensive study of many Australian woods not hitherto examined.¹³³ The soda process was employed, and trials made on a commercial scale showed that a number of eucalypts in particular gave very suitable pulps at an ultimate cost of about £10 to £12 per ton.

Several new processes for the isolation of cellulose are to be noted in which chlorine or its oxides are employed. J. F. Clerc¹³⁴ describes the De Vains method whereby bamboo, straw, etc. is treated with chlorine water, the solution, together with the bleaching powder subsequently necessary, being prepared on the spot from chlorine made by the electrolysis of salt. This has now been applied on an industrial scale.

¹²⁷ *Bull. Imp. Inst.*, 1922, **20**, No. 3; *Chem. and Ind.*, 1923, 432.

¹²⁸ *J.*, 1923, 546A.

¹²⁹ *Ibid.*, 1923, 493A.

¹³⁰ *Ibid.*, 1923, 447A.

¹³¹ *Ibid.*, 1923, 712A.

¹³² H. Kumagawa and K. Shimomura, *Z. angew. Chem.*, 1923, **36**, 414; *J.*, 1923, 924A.

¹³³ L. R. Benjamin, *Commonwealth of Australia, Inst. of Sci. and Ind., Bull.* No. 25, 1923; *J.*, 1923, 923A.

¹³⁴ *Papierfabr.*, 1923, **21**, 201; *J.*, 1923, 710A.

H. P. Waentig* and J. O. W. Gierisch¹³⁵ expose wood chips etc. after alkaline preparation, to an atmosphere of chlorine gas under a pressure of 6 atmospheres. The cellulose bleaches easily and gives solutions of high viscosity. F. Küttner, E. Sidler, and others¹³⁶ state that in such chlorinations the gaseous hydrogen chloride produced is never in a concentration greater than 10%, which makes it useless for technical purposes. By introducing an oxidising agent, such as ozone or hydrogen peroxide, with the chlorine, not only is the time of chlorination reduced, but the exit gas will contain as much as 20% of hydrogen chloride, which can be utilised.

In connexion with sulphite pulp attention may be directed to an important work by R. Lieckmann, "Die Fabrikation des Zellstoffes aus Holz Sulphitzellstoff," Elsner, Berlin, 1923.¹³⁷ The book is comprehensive and concludes with a description of the design and lay-out of a modern factory to produce 25 to 50 tons of pulp a day. On the engineering side of pulp production we note the scheme of A. Olier¹³⁸ for the digestion of fibrous materials, washing, bleaching, refining, and delivery to a paper-making machine in one continuous operation. All the chemicals used are recovered and regenerated electrolytically. The continuous digestion of fibrous materials under pressure is described also by R. Fournier,¹³⁹ and an economical process for grinding paper pulp by introducing compressed air into the stuff during admission to the beater by A. E. Ryberg and P. C. Schaanning.¹⁴⁰

Statistics showing the yields of cellulose and the consumption of material and power in the various processes are given by B. P. v. Ehrenthal.¹⁴¹

The influence of the grinding temperature on the properties of mechanical wood pulp has been studied by J. Teicher,¹⁴² who finds that as the temperature at which the pulp is ground increases, the tenacity of the paper made from it increases also. Maximum tenacity was obtained with pulp ground at 57° C., above which temperature a decided fall in tenacity took place.

Analytical methods for the control of sulphate and soda pulp mill processes are described by R. Sieber,¹⁴³ while the chemistry of the soda process for the production of pulp from aspen, loblolly pine, and jack pine has been carefully examined by S. D. Wells, R. H. Grabow, J. A. Staidl, and M. W. Bray.¹⁴⁴ Their maximum

¹³⁵ E.P. 178,196; *J.*, 1923, 10A.

¹³⁶ G.P. 370,346; *J.*, 1923, 650A.

¹³⁷ *Chem. and Ind.*, 1923, 756.

¹³⁸ E.P. 193,965; *J.*, 1923, 494A.

¹³⁹ *Paper*, 1923, 32, [5], 5; *J.*, 1923, 765A.

¹⁴⁰ E.P. 194,658; *J.*, 1923, 712A.

¹⁴¹ *Zellstoff u. Papier*, 1923, 3, 131.

¹⁴² *Papierfabr.*, 1923, 21, 153, 165.

¹⁴³ *Ibid.*, 1923, 21, 89; *J.*, 1923, 346A.

¹⁴⁴ *Paper*, 1923, 32, [9], 5; *J.*, 1923, 882A.

working pressure of 100 lb. is reached in 1 hour. After 2 hours 90% of the cooking has taken place, and from 15 to 30% of the cellulose originally present has been lost. Pentosans, in the case of aspen, decrease in amount during the first two hours, but then remain constant, indicating the presence of a resistant pentosan grouping in aspen wood. With the pine wood pulps beating tests show that drastic cooking with excess of soda leads to a high bursting strain and tensile strength. Long cooking with the smallest possible proportions of soda develops tearing and folding qualities. By the addition to the boil of 2 lb. of sulphur (to 100 lb. of wood)¹⁴⁵ the digestion is more rapid, the loss of cellulose is reduced, and the pulp is easier to disintegrate and bleaches with one-half the consumption of bleaching powder. Paper made from the sulphur-soda pulps gives greatly improved strength tests and tearing and folding values.

Another contribution to the chemistry of this process is furnished by S. S. Aiyar,¹⁴⁶ who has measured the distribution of methoxyl during cooking for various periods. He concludes that all the methoxyl is associated with lignin and that, with his conditions, cooking for longer than two hours is unnecessary from the point of view of the removal of non-cellulosic material.

In the case of sulphite pulp the factors affecting the quality and yield of pulp are discussed by B. Johnsen and H. N. Lee,¹⁴⁷ who point out that dense wood increases the capacity of the digester, allowing of longer cooking and lower temperature with an increased yield. Decay lowers the density of wood with diminished production. While most fungi causing decay diminish the cellulose, the fungus *Trametes pini* increases the cellulose content 15%, diminishing the lignin by 30%. E. P. Cameron¹⁴⁸ points out the important influence of pressure on the strength of test sheets prepared for testing pulp for strength, and states that this factor should always be specified.

In the matter of bleaching, some careful work by C. G. Schwalbe and H. Wenzl¹⁴⁹ on the bleaching of sulphite pulp may be noted. The ash of the bleached pulp was very much lower when the pulp had been drained and washed in the centrifuge, than it was with pulp drained without centrifugal action. A great advantage in time, quality, and yield was obtained by bleaching at 30°-35° C., preferably with free circulation of air. It was found that during bleaching there is a continuous formation of carbon dioxide, which, if not removed by heating and agitation (aeration), combines with

¹⁴⁵ *Paper*, 1923, **32**, [10], 5; *J.*, 1923, 882A.

¹⁴⁶ *Ind. Eng. Chem.*, 1923, **15**, 714; *J.*, 1923, 825A.

¹⁴⁷ *Pulp and Paper Mag.*, 1923, **21**, 111; *J.*, 1923, 304A.

¹⁴⁸ *Ibid.*, 1923, **21**, 127.

¹⁴⁹ *Papierfabr.*, 1922, **20**, 1625; 1923, **21**, 268; *J.*, 1923, 50A, 711A.

the calcium hydroxide present, forming bicarbonate. This substance acts as a "buffer" and gradually stops the bleaching action.

E. Heuser and W. Niethammer¹⁵⁰ find that by treating sulphite pulp first with chlorine water, then with dilute alkali, and finally with ordinary bleach liquor, the total amount of chlorine required is only one-half of that required with the ordinary bleaching powder bleach.

WASTE LIQUORS.

The important problem of the concentration of waste liquors is fully considered by K. L. Thunholm,¹⁵¹ who describes the working of the heat-pump system.¹⁵² The evaporation takes place in thin annular layers, so that the vapour pressure of the liquid at the evaporating surface is practically the same as that at the heating surface. The whole design is based upon working at the smallest possible temperature difference, so that the temperature increase imparted by the compression pump to the vapours may be kept down to a minimum.

By treatment of concentrated sulphite cellulose lyes with chlorine gas A. Schmidt¹⁵³ obtains compounds containing 20–30% of chlorine suitable for tanning materials or resin substitutes. M. Melamid,¹⁵⁴ by a process of hydrogenation, converts a liquid resin, "talloel," produced in the sulphate process, into a substitute for fatty acid oleins for the treatment of textiles.

A large number of communications deal with the analysis of waste liquors. Thus R. Sieber¹⁵⁵ gives a very full and practical account of the analytical methods needed for the control of sulphate and soda pulp mills, which should be read by those interested, and also a method for the determination of bases in sulphite liquors prepared from dolomite.¹⁵⁶ A. Sander¹⁵⁷ notes that calcium sulphate is very much more soluble in sulphite lyes than in water, some samples of lye containing as much as 4 grams per litre; he gives a method for its determination. For the determination of sugar in sulphite liquors M. Kleinstück¹⁵⁸ recommends the use of an alkaline mercuric cyanide solution as simple and convenient.

An increased production of alcohol by the fermentation of sulphite cellulose waste lyes is claimed by C. Jacoby,¹⁵⁹ if absorbent

¹⁵⁰ *Papierfabr.*, 1923, 21, *Fest u. Auslandsheft*, 52; *J.*, 1923, 924A.

¹⁵¹ *Svensk Pappers Tid.*, 1922; *Papierfabr.*, 1922, 20, 1774; *J.*, 1923, 179A.

¹⁵² E.P. 156,592; *J.*, 1922, 163A.

¹⁵³ E.P. 178,104; *J.*, 1923, 765A.

¹⁵⁴ E.P. 170,502; *J.*, 1923, 22A.

¹⁵⁵ *Papierfabr.*, 1923, 21, 89; *J.*, 1923, 346A.

¹⁵⁶ *Ibid.*, 1923, 21, 235; *J.*, 1923, 710A.

¹⁵⁷ *Chem.-Zeit.*, 1923, 47, 336; *J.*, 1923, 493A.

¹⁵⁸ *Zellstoff u. Papier*, 1923, 3, 51; *J.*, 1923, 493A.

¹⁵⁹ G.P. 310,318; *J.*, 1923, 546A.

substances, such as kaolin, humin, etc., be added to the lyes before neutralisation and filtration. E. Hägglund¹⁶⁰ has also studied the production of alcohol from these liquors. He finds that during fermentation a hydrogen-ion concentration of p_H 4·0–4·5 is maintained and this is irrespective of the initial hydrogen-ion concentration of the liquid. The optimum for alcohol production is p_H 5·0–6·0, the yield of alcohol varying from 0·5 to 0·8 gram per 100 c.c. As is well known, this alcohol contains acetaldehyde, and Hägglund states that the amount of this depends upon the hydrogen-ion concentration before fermentation begins, the quantity formed increasing up to a certain point as this initial concentration increases. A. W. Owe¹⁶¹ notes that a sulphite spirit gave on fractionation a product b.p. 101°–102°, which consisted almost entirely of acetal.

PAPER.

The problems associated with sizing have been exhaustively dealt with by W. Ostwald and R. Lorenz,¹⁶² who from sodium resinate obtain a γ -pinic acid m.p. 75° C. Dehydration of this leads ultimately to an abietic acid m.p. 161°, so that there exists a series of acids varying in hydration between these two well-defined substances. Possible sizing media are comprised between neutral sodium abietate and the colloidal hydrosol of abietic acid. The latter shows the properties of a suspensoid, and commercial size "emulsions" are shown to be really suspensions of abietic acid in its molecularly dispersed sodium salt. Both colloidal abietic acid and paper pulp are shown to be negatively charged, so that a permanently sized paper cannot be made by precipitating the size with acids alone. Permanency is secured when the condition is isoelectric, i.e., when the positive charge of the aluminium hydroxide present is equal to the negative charges of the abietic acid and the pulp. In the hollander the sulphuric acid liberated from the aluminium sulphate balances the peptising influence of the sodium hydroxide from the sodium resinate. Very interesting observations on the flocculating effect of electrolytes on abietic acid and the influence of various additions, such as casein, are described in these interesting communications, which are an excellent example of the application of refined scientific technique to a commercial problem of high importance.

N. D. Ivanoff¹⁶³ has also studied the hydrolysis of rosin size emulsions. His results show that the more dilute the size emulsion the more complete is the hydrolysis of the sodium resinate. An

¹⁶⁰ Zellstoff u. Papier, 1923, **3**, 183; J., 1923, 993A.

¹⁶¹ Papierfabr., 1922, **20**, 1564; J., 1923, 25A.

¹⁶² Kolloid-Zeits., 1923, **32**, 119, 195; J., 1923, 347A, 396A.

¹⁶³ Zellstoff u. Papier, 1923, **3**, 76; J., 1923, 711A.

emulsion containing normally 40% of free rosin at a dilution of 1 part in 2000 (approximately the dilution in the beater) was so altered by hydrolysis that 95.5% of the rosin existed in the free state, although in the presence of excess of sodium hydroxide.

On the technical side we note claims for the application of montan wax emulsions as giving a uniform sizing,¹⁶⁴ and the use of neutral or basic aluminium chloride as an efficient and cheap substitute for the sulphate in resin sizing.¹⁶⁵

¹⁶⁴ H. T. Bohme, A.-G. Chem. Fabr., G.P. 364,000; *J.*, 1923, 447A.

¹⁶⁵ Chem. Fabr. Griseheim-Elektron, G.P. 363,668; *J.*, 1923, 447A.



BLEACHING, DYEING, PRINTING, AND FINISHING.

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THE industries represented by this section, in common with many others, have suffered from financial stringency and bad trade during the past year, and this condition of things is naturally unfavourable to the rapid development of inventions and improvements entailing large outlay.

Its many sub-divisions, and intense specialisation along narrow lines, coupled with large output, are the chief characteristics of the British textile industry, in marked contrast with those of most countries. These characteristics lend themselves to the introduction of secret improvements which may evade any mention in technical literature for a long time ; most of them, perhaps, are not of a very high order of invention, considered as ideas, but in practice, when coupled with large productive capacity, they are capable of yielding in the aggregate a considerable advance, due to a steady increase in the standard of technical performance, already high, and thus becoming almost imperceptibly higher as time passes. The powerful combinations connected with these industries are by no means favourable to publicity as regards their technical methods, and, generally, among trusts, firms, and individuals, specialised technical knowledge and technical skill are more strictly guarded and jealously conserved than is commonly assumed.

With the advent of the Research Associations, and a greater tendency to regard chemists as desirable, if not yet entirely necessary items of equipment, there is a greater likelihood that patent and technical literature will become more scientific, representative, and reliable as a record of progress. It is important to remember, however, that a long time must yet elapse before anything like the standards of judgment applicable to work in the domain of pure chemistry, or even in industries which depend on known chemical reactions and deal with well-defined products, can be adopted for use in this field, where limitations to the application of scientific knowledge and method abound, owing to the very incomplete knowledge we possess of the principal materials, and the arbitrary standards of taste and requirement for which these industries cater. The technical importance of new work in this

field, as in others, depends in the last analysis on the production of wealth, and chemistry is only a part, and often too small a part, of the equipment. It is almost impossible to convey to the pure chemist a due appreciation of the work which is usually accounted greatest in this field. One has only to think in this connexion of the technical significance of Lowe's stretching of cotton while under the well-known influence of caustic soda, or Schreiner's particular modification in the use of an engraved calender. As scientific inventions, neither can be rated high; as technical inventions, both were revolutionary. The real skill and intellectual effort of the inventor are demanded for improvising the new technique for rendering his ideas assimilable by one of these industries. "Whoever invented the spinning, Arkwright certainly had the merit of performing the most difficult part, which was the making it useful" (James Watt, in a recently published letter).¹

Most textile chemists are familiar with the apparent lack of novelty in many patents and also much that appears as claiming originality in the technical literature. In many cases these claims to notice are made in ignorance of what is known elsewhere. In certain other cases they may represent an attempt to obtain some measure of protection or priority claim for a real achievement, such as the "making useful" of some known but hitherto impracticable idea. A satisfactory patent involving improvements in textile-chemical processes is usually difficult to draft, and in some branches, e.g., mercerising, incurs often so many disclaimers as to make it almost impossible to obtain protection for what may be, in fact, a new and practical process.

First-rank discoveries and "key-patent" inventions are of rare occurrence in the industries covered by this report, the promoting causes of what visible changes there are being usually not far to seek. If the *bona-fide* first-rank originator is not conspicuous in the ordinary year's report, there are, however, important places in these industries both for the research chemist's patient investigations and the technical chemist's skill in overcoming obstinate economic and technical difficulties in the way of "making useful" a great many conceptions which previously have failed to justify their adoption in practice. Literary distinction and academic honours fall most often to the successful research chemist in this, as in other fields. The triumphs of the technical chemist more often are reflected in balance sheets, by the state of which most of his work must be governed. The writer cannot hope in this report to conceal altogether a technical chemist's bias of the kind exhibited in the above quotation from James Watt, who laid the foundation of modern bleaching methods in this country, by "making useful" some well-known properties of chlorine.

¹ Glasgow Herald, Oct. 19th, 1923.

SCOURING AND BLEACHING.

In connexion with this branch of textile chemistry, it should be noted that P. H. Clifford and R. G. Fargher² have investigated the volatile products from American cotton treated with water and also with 2% caustic soda at 40 lb. pressure. In both cases acetone was a principal ingredient in the distillate, and in the latter case methyl alcohol also, from which it is suggested that pectin is present in cotton.

In a noteworthy paper,³ R. G. Fargher and M. E. Probert describe a study of the constituents of a benzol extract of American cotton. The work is of great interest in respect of the variety and character of the many constituents identified in the wax obtained, including a new alcohol, gossypyl alcohol, as the principal constituent. The value of the work, however, appears to have been depreciated unnecessarily by the use of an extraction apparatus into which live steam was blown during extraction. The writer has worked solvent extraction on a large scale for several years, as an adjunct to the bleaching and finishing of cotton and linen cloth, and may say that this extraction method could not give anything like a full yield of extracted wax, and the authors' figures showing only 8 lb. of wax from two tons of cotton confirm this view. While the value of the research must have been greater if the whole of the wax available had been extracted and used for the investigation, the extent of saponification and chemical change also caused by the presence of live steam is unknown, but must have been considerable. Further evidence that mechanical and chemical disintegration of cotton result in increased yields of extract with organic solvents is provided by E. Knecht and B. H. Streat.⁴

The writer has contributed a further paper⁵ on the only large-scale introduction of solvent extraction in connexion with the bleaching and finishing of cotton and linen cloth which has yet achieved continuous working and economic justification. The paper was written under obvious restraints, and the writer has no means of knowing whether its contents are worth more than mere mention here.

With the exception of the work of P. H. Clifford and R. G. Fargher, mentioned already,² there is little connected with ordinary boiling to report. The limits of treatment on the lines of increasing pressure and temperature have long ago been reached, without an understanding of what actually takes place to produce the improvements thus gained having been obtained. In the paper⁵ referred to, the writer claimed that the presence of undecomposed nitro-

² *J. Text. Inst.*, 1923, **14**, 117T; *J.*, 1923, 709A.

³ *Ibid.*, 1923, **14**, 49T; *J.*, 1923, 263A.

⁴ *J. Soc. Dyers and Col.*, 1923, **39**, 73; *J.*, 1923, 345A.

⁵ M. Fort, *ibid.*, 1923, **39**, 42; *J.*, 1923, 220A.

genous matter in kier liquors, throughout the boil, indicates that priority in importance should be assigned to the dissolving action of the alkaline liquors during the boil, over their decomposition of the nitrogenous matter with elimination of nitrogen, although the kier boil acts in both ways. The writer finds it possible, along other lines than those of orthodox scouring, to obtain complete removal of nitrogen without any boiling of either linen or cotton. A system of laundering has been protected in which most of the soap ordinarily used is replaced by a soluble phosphate.⁶ If laundries can be induced to adopt such mild methods, at a greater cost, the work of the bleacher's chemist in investigating cases of damages which sometimes appear in goods after a period of use, will be greatly reduced. Similar reasons exist for interest in the recent controversy among German textile chemists, produced by P. Heermann's advocacy^{7,8} of a more extensive use by laundries of limited bleaching treatments, with hypochlorites or ozone, in place of the much-favoured hot alkaline soap-bath, containing "per-compounds" to promote oxidation, which is stated to be twice as destructive in practice as Heermann's bleaching treatments. W. Kind⁹ and others¹⁰ have upheld the use of "per-salts" and criticised Heermann's conclusions. The writer has had ample evidence of the destruction of cotton and linen in laundries by the hot alkaline "per-salt" treatment, and may instance cases in which linen has decreased 40% in weight under this treatment, during a period of use which should not have caused a third of this loss. Copper figures cannot reflect adequately the progress of this kind of damage, as the products of oxidation are dissolved in the hot alkali as they are formed and attenuation of the fabric proceeds steadily with no very obvious signs of injury, except decrease in weight and strength. On the other hand, the introduction of stronger bleaching agents into laundry practice would lead to still greater abuse of fabrics, as the skill for their proper use is wholly lacking at present. Heermann's statement that linen is more susceptible to deterioration than cotton is absurd as regards rational usage. One reason for the greater durability of linen is that dirt is far less persistently retained against washing than in the case of cotton, and a more limited mechanical treatment, therefore, suffices to cleanse it.

Qualitative tests for distinguishing the per-reagents used in washing powders are given by A. Blankart.¹¹ A filtration

⁶ R. H. Plair, U.S.P. 1,435,332; *J.*, 1923, 53A.

⁷ P. Heermann, *Z. angew. Chem.*, 1923, **36**, 101; *J.*, 1923, 306A.

⁸ P. Heermann and H. Frederking, *Textilber.*, 1922, **3**, 456; *J.*, 1923, 51A.

⁹ *Chem.-Zeit.*, 1923, **47**, 457; *J.*, 1923, 712A.

¹⁰ Ebner, *Z. angew. Chem.*, 1923, **36**, 323; *J.*, 1923, 767A.

¹¹ *Helv. Chim. Acta*, 1923, **6**, 233; *J.*, 1923, 390A.

method, providing a "carbon number," for use in estimating the detergent power of soaps, is described by J. W. McBain, R. S. Harborne, and A. M. King,¹² and F. E. Hartman has given interesting information about industrial ozone generators.¹³

As regards bleaching proper, an unusually detailed and accurate account of the methods mainly in use for bleaching yarns of flax and other bast fibres, is given by E. Clayton.¹⁴ An important consideration in this class of work is the loss of weight which accompanies the production of a particular standard of bleach. Linen ordinarily loses about 25–30% of its weight in bleaching to a full white, and this represents the wastage unavoidable in obtaining what is practically pure cellulose. Much has been written on the very real dangers of attempting to conserve the weight during bleaching by retaining a proportion of non-cellulose impurities. Textile chemists have been unanimous in regarding practically pure cellulose as the ultimate aim in bleaching cotton or linen white, to attain the valuable qualities reflected by a low copper figure, absence of nitrogen, low alkali solubility and ash content, and absence of wax, lignin, and traces of retained chemicals. During the year, however, a considerable departure from standard practice has led to the production of a type of bleached linen of good quality by the above tests, yet weighing 15% more than is usually the case.

From close association with the new product the writer can state that this extra weight is conserved from the original linen by selective removal of the non-cellulose constituents of linen, but the bleached product is of the highest class in respect of durability in use and low nitrogen, wax, lignin, and ash contents. The copper value and solubility in hot washing soda are low, but on treatment with boiling caustic alkalis a heavier loss in weight occurs without undue discoloration or wastage of cellulose. While no description of the method by which this result is obtained has been given, it may be said that the time was ripe for a departure from stereotyped bleaching methods, and during recent years signs have not been lacking of a desire to get away from the obsession that increased severity in kier-boiling was the foundation of progress in bleaching. Solvent extraction, from being a vague possibility, has become, in one works at any rate, a part of the bleacher's equipment for dealing perfectly, when desired, with unsaponifiable waxes, which no permissible kier-boiling could wholly remove. The use of pancreatic enzymes for elimination of nitrogenous matter and fats has been patented by O. Röhm,¹⁵ while de-sizing with malt and other diastatic preparations has long been incorporated into common

¹² *J.*, 1923, 373T. See also J. W. McBain, *Chem. and Ind.*, 1923, 615.

¹³ *J.*, 1923, 117T.

¹⁴ *J. Soc. Dyers and Col.*, 1922, 39, 31; *J.*, 1923, 220A.

¹⁵ E.P. 100,224: *J.*, 1916, 105.

practice. Continental bleachers have experimented considerably with bleaches short of full white, in which a considerable proportion of non-cellulose matter has been retained, and a succession of patents from abroad testifies to their continued interest in this matter. Their products, however, are usually characterised by inability to reach the standard claimed, or to withstand a careful comparison by means of the tests named, and in storage and use, alongside a pure cellulose product. Recent patents showing a tendency to avoid undue loss in weight in bleaching include those of C. Bochter,¹⁶ who claims to bleach linen, without the usual kier-boiling with alkalis, by boiling under pressure with dilute bisulphite solutions, followed by oxidation treatment of the usual type. Later, he has proposed to add volatile bases to the bisulphite solutions,¹⁷ and in another patent, to shorten the bleaching process for cotton by the use of 0·05-0·1% of sodium hydrosulphite added to caustic lye in kier-boiling.¹⁸

The perennial controversy on the inner mechanism of bleaching by means of hypochlorite baths, which bids fair to rival the theory of dyeing and the theory of the relation between constitution and colour, as a field in which perpetual warfare reigns and no complete victory is ever secured, has not resulted in much published work this year.

Bleaching, like dyeing, involves the interaction of known reagents with fibre-constituents about some of which very little positive information has been gained. Some experiments by which S. R. Trotman¹⁹ claimed to demonstrate the superior properties of hypochlorous acid over bleaching powder solutions, modified in various ways, when applied to cotton, have been criticised by R. L. Taylor.²⁰ Taylor maintains that the "hypochlorous acid" of Trotman contained a hypochlorite as well, hence the superior whites. Without endorsing all Taylor's views, the writer regards his work as of great importance. Although handicapped by his position of isolation from industrial practice, Taylor has been first to recognise certain distinctions in the behaviour of the different colouring-matter of fibres, and the great importance of undecomposed hypochlorite in stimulated bleaching-solutions—both matters of considerable practical importance.

A new patent,²¹ however, claims that the use of an excess of mineral acid for stimulating hypochlorite bleaching-solutions is justified, as it is found that the liberated hypochlorous acid bleaches faster than it decomposes to waste, so that an actual economy can

¹⁶ E.P. 180,325; J., 1923, 546A.

¹⁷ E.P. 187,575; J., 1923, 713A.

¹⁸ E.P. 182,776; J., 1923, 971A.

¹⁹ J., 1923, 2t.

²⁰ J., 1923, 79t.

²¹ Zellstoff-fabrik Waldhof, G.P. 371,398; J., 1923, 651A.

be gained by over-acidification. The use of liquid chlorine has extended in the paper trade, where consumption is large, but bleachers of textiles have not yet shown much eagerness to adopt this article for use. The greater convenience offered by liquid chlorine is largely offset by the cost and greater risks attached to its use, and the necessity for some outlay before adopting it. Several new patents bearing upon its use are as follows : one for production of bleaching liquor from milk of lime,²² a chlorinating apparatus²³ of noteworthy construction, a proposal to effect chlorination of alkalis while passing through a centrifugal pump,²⁴ and a closed chamber apparatus with wagon containers in which fibres can be treated with a gas under pressure.²⁵

E. Knecht and J. P. Egan²⁶ have contributed data relating to the loss in strength, copper number, and oxygen consumption of cotton treated with solutions of hypochlorous acid, bleaching powder, and permanganate. When originally proposed as an index figure for bleached cellulose fibres by Schwalbe, it seemed as though the copper value would prove to be of the greatest use, especially to the bleacher's chemist. It is now becoming apparent that while the copper figure, when high, may give positive evidence of great value, its value as negative evidence when low is much less, unless it be coupled with full knowledge of how far the products of oxidation of cellulose, which a copper figure should represent, have suffered removal by the action of alkali, which may be effective enough even in a solution of bleaching powder to affect the copper figure adversely. The writer long ago imposed severe limitations upon his own use of, and deductions from, copper values, which are most simply "present state of oxidation" values, and any fuller extension of significance requires a great deal more care than is commonly given before it can be accepted. The Methylene Blue test for over-bleaching may fail also owing to intervening alkaline action having removed the oxidised matter. The fault of such wrong interpretations lies of course more with the individual than with the test; but what is wrong when one may search the literature without gaining any very clear ideas as to what distinction can be made between the behaviour of hydrated cellulose, "hydrocellulose" and "oxycellulose" towards Methylene Blue?

C. Birtwell, D. A. Clibbens, and B. P. Ridge²⁷ now state also that the extent of absorption of Methylene Blue by cotton depends on the fibre's origin, and the content and alkalinity of its ash. Hence

²² Chem. Fabr. Griesheim-Elektron, G.P. 368,891 ; *J.*, 1923, 397A.

²³ J. W. Van Meter, E.P. 201,214 ; *J.*, 1923, 926A.

²⁴ J. T., and J. Brandwood, E.P. 196,708 ; *J.*, 1923, 601A.

²⁵ D. and G. McIntosh, E.P. 200,122 ; *J.*, 1923, 826A.

²⁶ *J. Soc. Dyers and Col.*, 1923, **39**, 67 ; *J.*, 1923, 349A.

²⁷ *J. Text. Inst.*, 1923, **14**, 297T ; *J.*, 1923, 1066A.

the scouring treatment given in bleaching affects the absorption of this dye, while residues of protein, pectic matter, soap, and oleine increase absorption. There is great need of better tests, and an important discovery by A. E. Everest and A. J. Hall²⁸ appears likely to lead to a more useful means of distinction than has hitherto been available for "oxycellulose," which, it appears, develops a strong coloration when treated with tetrazotised benzidine in presence of alkali, while "hydrocellulose" reacts very little, and normal cellulose and mercerised cellulose not at all. No doubt variations in the amount of alkali, and other conditions, such as impurities in the fibres, will affect the results, but there seems no reason why this test should not be improved to give at least approximately quantitative results, and perhaps something much better than anything we have now could be evolved out of it, to the great benefit of all who deal with cellulose fibres.

Peroxide bleaching is more extensively used in laundering, and for bleaching of wool, than in competition with hypochlorites, but it has uses in many connexions, and an interesting description of suitable methods and apparatus is given by I. K. Weber.²⁹ It has been patented to use nickel, where metal is required in the construction of apparatus for peroxide bleaching,³⁰ and to bleach wool by means of peroxides by immersion, squeezing and letting lie, and stoving without washing.³¹

There is no important new feature to record in connexion with the scouring and bleaching of wool or silk.

S. H. Higgins has contributed a series of historical papers relating to the development of bleaching,³² and J. F. Corrigan a paper³³ in the same category, to which there are few contributors.

MERCERISATION AND ALLIED PROCESSES.

A useful review of the literature relating to this subject has been made by D. A. Clibbens,³⁴ one relating to lustring in general by A. Adderley³⁵ and another dealing with the swelling of cotton cellulose by G. E. Collins,³⁶ all these being part of the work of the British Cotton Industry Research Association. A lecture by G. Tagliani³⁷ also covers a good deal of the same ground.

²⁸ *J. Soc. Dyers and Col.*, 1923, **39**, 47; *J.*, 1923, 219A.

²⁹ *Ibid.*, 1923, **39**, 209; *J.*, 1923, 826A.

³⁰ Deutsche Gold u. Silber-Scheideanstalt and A. Schaidbauf, E.P. 188,811; *J.*, 1923, 52A.

³¹ D. and G. McIntosh, E.P. 196,003; *J.*, 1923, 546A.

³² *J. Text. Inst.*, 1923, **14**, 209, 277, 319, and 441T; also *Chem. and Ind.*, 1923, 1026.

³³ *J. Soc. Dyers and Col.*, 1923, **39**, 277.

³⁴ *J. Text. Inst.*, 1923, **14**, 217T.

³⁵ *Ibid.*, 249T.

³⁶ *Ibid.*, 264T.

³⁷ *J. Soc. Dyers and Col.*, 1923, **39**, 340.

Of new work, that of C. P. Nodder and R. W. Kinkead,³⁸ dealing with the mercerisation of flax and other bast fibres, is a noteworthy contribution from the Flax Industry Research Association. The literature has hitherto proved inadequate to explain satisfactorily the almost complete failure to apply mercerisation to linen in practice, and in view of this failure the writer announced³⁹ some time ago that he was working a process of mercerisation on linen damasks with complete success, the same process being still in regular use for producing a high lustre of permanent character. The conclusion reached by Nodder and Kinkead is that while it is possible to obtain flax fibres with a high lustre by mercerisation, the production of a linen fabric of high lustre is rendered difficult on account of the impossibility of avoiding the production of spiral ridges (they reject Huebner and Pope's theory of lustre) and the difficulty of preserving sufficient parallelism of the fibre. The writer agrees in the main with this statement of the difficulties, but they have in fact been largely overcome in the process referred to. The extra cost of mercerisation of linen is amply justified by the lustrous effect enduring throughout long wear, but in the present depressed state of the linen trade any extra cost is liable to create dismay.

A good deal of work during the last year or two has been devoted to ascertaining more minutely the changes involved by mercerisation of cotton, and determining the most favourable conditions. H. F. Coward and L. Spencer⁴⁰ have studied the ability of cotton to retain caustic soda solutions against centrifuging and shown more of the stronger solutions to be retained, mainly within the fibre. The same authors⁴¹ have observed that the greater absorption of lye by loose cotton than by fabrics is due to mechanical resistance to swelling in the latter case. No evidence of a definite compound was considered to be gained in spite of the greater ratio of caustic soda to water in the absorbed portion of lye, and the marked hysteresis in shrinkage during washing. G. E. Collins and A. M. Williams⁴² have studied the behaviour of cotton hairs in caustic soda solutions, and H. K. Corser and A. J. Turner have contributed the first instalment of a detailed study of the influence of the degree of twist in yarns upon the results of yarn mercerisation, and fabrics made from these yarns.⁴³ Among other provisional conclusions reached, it is stated that increased frictional resistance between the fibres probably explains any increase of strength shown after mercerising.

³⁸ *J. Text. Inst.*, 1923, **14**, 133T; *J.*, 1923, 766A.

³⁹ M. Fort, *J. Soc. Dyers and Col.*, 1921, **37**, 161; *J.*, 1921, 467A.

⁴⁰ *J. Text. Inst.*, 1923, **14**, 28T; *J.*, 1923, 221A.

⁴¹ *Ibid.*, 1923, **14**, 32T; *J.*, 1923, 221A.

⁴² *Ibid.*, 1923, **14**, 287T; *J.*, 1923, 1066A.

⁴³ *Ibid.*, 1923, **14**, 332T; *J.*, 1923, 1173A.

With regard to mercerising plant there is little new to report. W. Moscrop⁴⁴ has modified his apparatus for recovery of lye from fabrics, so that they now traverse a zig-zag path, subjected to alternate steam-jets and water-spirits. Commercial mercerising depends very largely for its profits on recovery of lye, for re-use after concentrating, or for use in boiling, or other ways. The method by which H. Gresham⁴⁵ eliminates the use of a stenter in mercerising, is on this account of no practical value. The use of alcohol as a penetrating agent for use in connexion with mercerising has long been known. A new patent,⁴⁶ however, claims the addition of alcohol to mercerising, dye and other liquors, applied to cotton, to increase penetration, while another⁴⁷ applies the slot principle to impregnation with lye, and in another⁴⁸ the strength of mercerising lye is reduced to one-third, with the addition of glycerin and sodium chloride.

Great activity has been shown in the last few years in patenting processes allied to mercerisation, by which it is claimed that some special effect like wool, glass, linen, silk and so on, is produced on cotton. All known reagents for obtaining hydration of cellulose have been or are being tried to secure some new effect. The well known parchmentising action, with production of amyloid, of sulphuric acid on cotton, has been studied with a specially close attention to detail, and the Swiss firm of Heberlein and Co., which led a revival of interest in this type of specialised treatment, has obtained further patents this year. Several years ago the writer experimented with acid treatments of cotton, from the point of view of increased lustre, linen-like effects of a permanent character, and superior finishing properties as regards beetling and other mechanical treatments. Much more effective removal of projecting hairs is obtainable than singeing can give, and a "lisle thread" finish can easily be developed. Chintz-like and stiff translucent finishes, with good closing of interstices and semi-permanence to washing, are also easily obtained. Exact control is very difficult in practice, however; there is more or less severe wastage of fibre substance involved, while the effects are often harsh and although distinct, did not prove attractive on the kind of goods most interesting to the writer. The desirability of imitating, more or less imperfectly, wool or linen is very dependent on the price of real wool and linen, and the class of fabric treated. Heberlein and Co.⁴⁹

⁴⁴ E.P. 196,753; *J.*, 1923, 601A.

⁴⁵ *Bull. Soc. Ind. Mulhouse*, 1923, 89, 198; *J.*, 1923, 651A.

⁴⁶ Fine Cotton Spinners Assoc., and M. Cunningham, E.P. 202,057; *J.*, 1923, 972A.

⁴⁷ E. Farrell, E.P. 197,358; *J.*, 1923, 651A.

⁴⁸ E. O. Sanner, G.P. 376,541; *J.*, 1923, 972A.

⁴⁹ E.P. 191,203; U.S.P. 1,439,512/520; *J.*, 1923, 180A. E.P. 192,227; *J.*, 1923, 306A.

now obtain transparency and lustre by mercerising, e.g., at 12° C., followed by a treatment with sulphuric acid (sp. gr. 1·58). Re-mercerising may follow, and is able to remove harshness. Wool-like effects are obtained by treatment with sulphuric acid (sp. gr. 1·515-1·546), then mercerisation under tension. Linen-like effects (on threads not exceeding 80 count) are obtained by treatment with caustic soda of sp. gr. over 1·116, below 0° C., followed by treatment with sulphuric acid. Textil Werk Horn A.-G.⁵⁰ add ammonium salts to sulphuric acid used for rendering cotton fabrics transparent, and thus avoid the usual unpleasant stiffness. A patent has been granted⁵¹ for obtaining a permanent finish on cotton by the use of nitrating acid, and another⁵² claims to obtain a transparent effect by using carbon tetrachloride along with caustic alkali, followed by a treatment with sulphuric acid of sp. gr. 1·6-1·7.

Recent interest in the use of calcium thiocyanate as a solvent for cellulose is reflected in a patent⁵³ for obtaining mercerisation with this reagent, without the usual harshness, by mercerising in the ordinary way before, or after, the thiocyanate treatment, which is applied also to printing.

DYEING OF VEGETABLE FIBRES AND ARTIFICIAL SILKS.

The most important and interesting work of the year under this section relates to the dyeing of cellulose acetate silk. It is matter for congratulation that, while it is only recently this fibre has become a British manufacture, and whereas long previously it had gained the close attention of one of the great German dyestuff firms, the invention of satisfactory dyes capable of being applied to it by simple practical methods, is of British origin. The resultant simplification of treatment and extension of use should go far in helping to ensure the success of acetate silk. It is likely, however, that acetate silk, as we now know it, will sooner or later be displaced by a new or improved product with less tendency to revert under alkaline and other influences, with accompanying loss of lustre. The present type of acetate silk is no improvement on the other artificial silks for use in conjunction with linen or cotton to be bleached in the piece, for while it withstands the dissolving action of an alkaline treatment better, it readily undergoes saponification and loses lustre under conditions which damage the lustre of certain other artificial silks very little. It is noteworthy that

⁵⁰ E.P. 195,620; *J.*, 1923, 884A.

⁵¹ C. L. Schuttig, U.S.P. 1,451,306; *J.*, 1923, 547A.

⁵² J. McHaffie, and Stevenson, McKellar and Co., E.P. 189,968; *J.*, 1923, 92A.

⁵³ Calico Printers' Assoc. and E. A. Fourneau, E.P. 190,896; *J.*, 1923, 601A.

there is patent activity, both in this country and abroad, in connexion with alkylcelluloses and other cellulose products as spinning materials, and the artificial fibre industry is now capable of quick developments. Meanwhile cellulose acetate silk with its soft lustre, low inflammability, and insolubility, with consequent greater strength when wet, seems likely to attain considerable use and occupy an important place in the textile industry. The same quality of insolubility, or resistance to wetting, has been the obstacle to dyeing it by ordinary methods. Two obvious solutions of the difficulty have been exploited for some time, *viz.*, to add dyes to the solutions used for spinning, and, alternatively, partially to saponify the acetate silk as an operation preliminary to dyeing in aqueous baths. Both methods have certain pretty obvious drawbacks and tend to limit the uses of the product. The search for more satisfactory methods has centred chiefly on improving the application of the ice-colours, and alternatively producing from insoluble azo dyestuffs a class of derivatives which the fibre could take up from aqueous solutions. It is success along the latter lines which provides the outstanding achievement in dyeing this year.

A. G. Green, K. H. Saunders, and British Dyestuffs Corp.,⁵⁴ claim the manufacture and use as dyes for acetate silk, of ω -methyl-sulphonic acids of amino-azo compounds, these dyes possessing the special property of liberating their coloured bases for gradual absorption by the fibre. Diazotisation of these dyes on the fibre, and development in the usual way with phenolic compounds, yields still greater variety in shades, as well as increased fastness. The harmful preliminary saponification treatment with alkalis is rendered thereby unnecessary, and complicated colloidal and other variations of the usual dyeing methods are likely to be superseded by simple, easily controlled dyeing operations. A further achievement is recorded in the patent⁵⁵ of J. Baddiley, J. Hill, and E. B. Anderson, along with British Dyestuffs Corporation. Unlike sulphonic acid compounds, which form the great majority of ordinary water-soluble dyes, certain water-soluble dyes containing carboxyl groups are suitable for dyeing acetate silk. This simple distinction apparently has been long overlooked by an army of experimenters. The distinction is easily made if dyeing of the water-resistant fibre is regarded as analogous to the transference of a dissolved substance from one solvent to another immiscible solvent. The discovery leads direct to the production of a wide range of shades, obtainable by simple dyeing of amino-carboxylated dyestuffs, with possibilities of diazotisation on the fibre and development along the usual lines of practice.

⁵⁴ E.P. 200,873; *J.*, 1923, 926A.

⁵⁵ E.P. 202,157; *J.*, 1923, 972A.

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⁵¹ C. L. Schuttig, U.S.P. 1,451,306; *J.*, 1923, 547A.

⁵² J. McHaffie, and Stevenson, McKellar and Co., E.P. 189,968; *J.*, 1923, 92A.

⁵³ Calico Printers' Assoc. and E. A. Fourneau, E.P. 190,896; *J.*, 1923, 601A.

The Chem. Fabr. Griesheim-Elektron⁷⁰ protects the use of 4-halogen-3-toluidide of 2,3-hydroxynaphthoic acid for use in the production of fast shades on cotton, of the insoluble azo type which yields such notable advances on what was formerly obtainable with a β -naphthol prepare. This new series of preparing agents of the Naphthol AS class is now able to provide a fairly wide range of shades, fast to boiling and chlorine. These two qualities are not enough, however, to satisfy the bleacher and finisher of piece goods containing dyed effects. The writer has bleached goods containing coloured effects dyed with the new insoluble azo dyes, which are remarkably fast to hypochlorites, but they vary as regards the effect of alkalis and rubbing. Beetling is a severe test as regards rubbing, and if dyemakers and dyers would wrap their dyed samples in white cotton and hammer or beetle them for an hour under varying conditions of damp, they would surely modify some of the claims made to fastness to rubbing. It is now claimed to improve the fastness to rubbing of the ice and developed dyes by applying strong suction to fabrics while wound on a perforated beam, after developing.⁷¹ In connexion with the same class of dyes, a paper by J. Rath⁷² on the colloidal state of Naphthol AS in the alkaline grounding or preparing solution used in dyeing, is of considerable practical and scientific interest.

In connexion with mordanting, claim is made⁷³ to apply colloidal solutions of metallic salts of sulphonated coumarone resins. A paper by C. Sunder⁷⁴ deals with the use of antimony compounds for fixing tannins, and A. Peltzer discusses the evaluation of tannins for use in dyeing.⁷⁵ A careful comparison by means of actual trials is still far more reliable for examination of tannins for use in dyeing than any system of chemical analysis. A method of synthesising a blue dye *in situ* on tannin-mordanted cotton consists of steeping in an oxidising bath, followed by a bath of colloidal sulphur and an alkylated *p*-phenylenediamine salt.⁷⁶ An improved method of dyeing logwood blue on cotton,⁷⁷ a proposal to add dyes to the oil softening-liquor applied to jute in batching,⁷⁸ and a method of improving the quality of blue pigment obtained as a by-product from prussiate Aniline Black dyeing, by precipitating waste liquors with iron,⁷⁹ may also be mentioned.

⁷⁰ E.P. 201,712; *J.*, 1923, 968A.

⁷¹ Chem. Fabr. Griesheim-Elektron, G.P. 368,734; *J.*, 1923, 448A.

⁷² *J. Soc. Dyers and Col.*, 1923, 39, 334.

⁷³ H. Renner u. Co., A.G., E.P. 173,757; *J.*, 1923, 465A.

⁷⁴ *Bull. Soc. Ind. Mulhouse*, 1923, 89, 191; *J.*, 1923, 651A.

⁷⁵ *Chem.-Zeit.*, 1923, 47, 165; *J.*, 1923, 495A.

⁷⁶ H. Bergerich, G.P. 364,580; *J.*, 1923, 264A.

⁷⁷ H. Sunder, *Chim. et Ind.*, 1922, 8, 702; *J.*, 1923, 11A.

⁷⁸ Jute Industries, F. D. S. Sandeman, and G. B. Craddock, E.P. 203,258; *J.*, 1923, 1066A.

⁷⁹ Silver Springs Dyeing Co., and A. J. Hall, E.P. 188,208; *J.*, 1923, 11A.

A novel proposal is that of using azulmic acid, obtained by polymerisation of hydrocyanic acid, as a dye for vegetable fibres,⁸⁰ but its commercial success is doubtful. In connexion with dyeing machinery there are several new patents, but they do not appear to require description here.

Cases of industrial poisoning are not very often met with in the dyeing industry, outside a few special operations. The subject is one regarding which there has been a marked increase in the sensitiveness of public opinion in recent years, and greater precautions are likely to be demanded. R. Williamson reports on the poisoning of those employed in Aniline Black dyeing by the various methods.⁸¹ A patent has been obtained for "heading" certain kinds of dyed yarns in the damp state after dyeing, to avoid poisoning by lead dust.⁸²

G. G. Clegg and S. C. Harland⁸³ have investigated neps in cotton, and their resistance to dyeing. Neps were found to consist of tangled masses of thin-walled hairs, such as are known to arise from the death of cotton seeds before maturity, and this leads the authors to recommend a more detailed physiological study.

J. Huebner and J. N. Sinha⁸⁴ have continued Huebner's work on the absorption of dyestuffs by cotton, and it now embraces the behaviour of the principal celluloses towards iodine and dyestuffs. An interesting side-issue is their discovery of the formation of iodoform when cellulose is treated with iodine and caustic alkali.

A. Gillet and F. Giot⁸⁵ have investigated various lines of after-treatment and impregnation after dyeing, designed to increase the fastness of dyed shades to light and exposure. They claim to have shown that auto-oxidation causes fading in many cases, and that protection by the use of anti-oxygenisers is possible. No practical method, however, emerges from this research, if cost is to be considered. After-treatment with copper salts, which is the most-used practical method available for increasing fastness to light, is often accompanied by change of shade due to lake formation. Using the same dye and various metallic mordants, it is often possible, according to the writer's experience, to trace a connexion between fastness to light and insolubility of the lakes formed. Finishing methods which produce an air-tight skin on dyed fibres are also effective in some cases in hindering fading, but the subject is extremely complex and no single theory of fading will explain adequately the fading of all the dyed shades which are now produced.

⁸⁰ G. S. Bohart, Assr. to G. H. Whittingham, U.S.P. 1,464,802/3 ; *J.*, 1923, 1016A.

⁸¹ *J. Ind. Hyg.*, 1923, 4, 507 ; *J.*, 1923, 546A.

⁸² A. Ashworth, E.P. 192,469 ; *J.*, 1923, 306A.

⁸³ *J. Text. Inst.*, 1923, 14, 125 ; *J.*, 1923, 709A.

⁸⁴ *J.*, 1923, 255T.

⁸⁵ *Comptes rend.*, 1923, 176, 1558 ; *J.*, 1923, 708A.

A method of analysing sodium hydrosulphite in presence of air is described by S. H. Wilkes,⁸⁶ and being based on a reaction with a mixture of potassium iodate and iodide, is only applicable in absence of certain impurities, and is, therefore, not applicable to the analysis of dye vats.

DYEING OF ANIMAL FIBRES.

The dyeing of animal fibres provides the chief battlefield for the exponents of various theories of dyeing, as the evidence of chemical action here is so strong that any theory which ascribes dyeing of these fibres and fastness of the dyed shades to purely physical causes of attraction between fibre and dye, must either ignore or endeavour to dispose of a good deal of counter-evidence. The more vague and generalised is the theory, the less use it is to the industry, and while, presumably, theories of dyeing should lead to some improvement in practice, it is undeniable that they very rarely do, but remain usually in the enchanted borderland between chemistry and physics, and are little heard of in dyehouses. It is important to bear in mind the heterogeneous chemical and physical nature of fibres and materials which are dyed, and likewise the heterogeneous character of the coloured products rated as dyes. As the writer has already pointed out elsewhere, sulphuric acid would be rated as a dye if it were coloured, for it is absorbed by wool and retained against washing, like picric acid, which is reckoned a dye. The accidental nature of colour in relation to absorption by fibres is overlooked in a good deal of hasty generalising about dyeing. Chemical knowledge relating to dyeing is always useful in practice, and, where it can be systematised to explain the main features of a dyeing operation, provides the most useful theory available for the dyer, while often undeniably leaving a good deal of the remoter changes taking place in dyeing to be explained in other ways.

F. E. Bartell and E. J. Miller⁸⁷ show that chemical change takes place involving considerable hydrolysis and liberation of alkali hydroxide, when acid dyes are absorbed by sugar charcoal free of ash. J. R. Adams⁸⁸ finds no difference in his experiments, between the "adsorption" of acid dyes by chlorinated and untreated wool, which is contrary to the accounts hitherto given in both patent and technical literature.

The "adsorption" of Orange II. by alumina is found to be largely affected by small changes in hydrogen-ion concentration,⁸⁹ while somewhat related are the observations of T. R. Briggs and

⁸⁶ *J.*, 1923, 3567.

⁸⁷ *J. Amer. Chem. Soc.*, 1923, 45, 1106; *J.*, 1923, 671A.

⁸⁸ *J. Phys. Chem.*, 1923, 27, 81; *J.*, 1923, 221A.

⁸⁹ O. Reinmuth and N. E. Gordon, *Ind. Eng. Chem.*, 1923, 15, 818; *J.*, 1923, 926A.

A. W. Bull,⁹⁰ who claim support for a physical theory of the dyeing of wool with acid and basic dyes, from experiments in which the amount of dye "adsorbed" was found to vary continuously with the hydrogen ion concentration. Every dyer is familiar with the fact that increased acidity of the bath promotes the dyeing of acid dyes, and retards that of basic dyes, but, *a priori*, this appears more like evidence of a chemical theory of dyeing than a physical theory. It would be interesting to know how the physical theory deduced by these authors would be applied to another case of the dyeing of wool with acid dyes which falls to be reviewed here. British Dyestuffs Corporation and W. E. Sanderson⁹¹ protect a method of dyeing acid dyes on animal fibres from a bath containing soap and ammonium salts, this procedure allowing of the simultaneous dyeing of vegetable fibres present with direct dyes. The writer has stated his views at length elsewhere,⁹² and also shown that the use of an ammonium salt, in place of a free acid, to promote the dyeing of acid dyes, does not involve an increase in hydrogen-ion concentration in the dye bath, the bath being in fact alkaline with ammonia, while dyeing is proceeding, the assistance rendered to dyeing being thus related, not to any acidity of the bath, but to the transference of acid from the ammonium salt to the fibre, quite in accordance with the writer's theory of what occurs to promote dyeing when free acid is used in the bath. From this explanation to the method now patented is a small step, as the alkalinity of soap is not sufficient to increase the alkalinity of the bath containing ammonium salt, to an extent which will prevent the vital reaction occurring. It appears therefore that a physical theory of dyeing based on relating "adsorption" of acid dyes by wool to hydrogen-ion concentration in the bath, is unlikely to be of much service when applied to practice, which is the ultimate test of theories. Further contributions from the standpoint of a physical theory are those of R. Haller,⁹³ who failed, however, to establish any relation between the state of dispersion in indigo vats of various kinds and the varying results the dyeings provided under subsequent fastness tests; secondly,⁹⁴ the same author records some experiments which aim at showing that wool is not an amphoteric substance, but is incapable of entering into chemical reactions in various dyeing processes.

The extreme sensitiveness of wool and other animal fibres to chemical influences during dyeing, however, is the reason for a number of patents for methods of protecting these fibres from the

⁹⁰ *J. Phys. Chem.*, 1922, **26**, 845; *J.*, 1923, 91A.

⁹¹ E.P. 194,143; *J.*, 1923, 448A.

⁹² M. Fort, *J. Soc. Dyers and Col.*, 1916, **32**, 33.

⁹³ *Textilber.*, 1922, **3**, 433; *J.*, 1923, 11A.

⁹⁴ *Z. ges. Textilind.*, 1922, **25**, 402, 411; *J.*, 1923, 600A.

action of alkalis. J. Morton and K. R. Wood⁹⁵ add lactic acid to prepared dye vats to reduce the caustic alkalinity to harmless proportions. It is also claimed to add sulphite-cellulose waste-liquor to sulphur dyebaths⁹⁶ and to chrome dye baths⁹⁷ for wool, while animal fibres are preserved against injury during alkaline treatment by addition of a wide range of aromatic compounds, including *p*-diamines, quinones, and hydroxy derivatives of benzene and naphthalene.⁹⁸ Other patents deal with the addition of decomposition products of proteins to dye baths⁹⁹ and alkali-soluble protein compounds of heavy metals, prepared from vegetable extracts, which precipitate gelatin and find applications in dyeing and printing.¹⁰⁰ A method of rendering animal fibres resistant to dyeing is applied to the dyeing of unions to preserve these fibres unstained, and consists of treatment with acetic anhydride and acetic acid in presence of a catalyst,¹⁰¹ while the same firm has protected the use of acetic esters of tannic acid in a similar connexion.¹⁰²

A batch of patents granted to Akt.-Ges. für Anilin-Fabrik., is concerned with fur dyeing by oxidation methods, which this firm has done much to develop, and which has now reached so high a state of perfection as to be very apparent to all in the hyphenated coney products now occupying such a prominent position among furs. The new patents cover the use of 2.7-dihydroxynaphthalene,¹⁰³ the same in conjunction with 4-amino- or 4.4'-diamino-diphenylamine,¹⁰⁴ 1.5-dihydroxynaphthalene,¹⁰⁵ substitution products of 4-aminophenol,¹⁰⁶ and tri- or tetra-amino derivatives of diphenyl, diphenylmethane, or *sym*-diphenylethane in conjunction with *p*-diamines.¹⁰⁷ Modern fur dyeing is related to the method of dyeing Paramine Brown on cotton, long familiar to printers. The fur dyer, however, works largely with hydrogen peroxide and other "per-compounds" and the process is usually very wasteful in chemicals, but good results will pay for expensive methods. A hair-dye has been patented on the same lines.¹⁰⁸

⁹⁵ E.P. 202,757; *J.*, 1923, 1017A.

⁹⁶ Akt.-Ges. f. Anilin-Fabr., G.P. 369,296; *J.*, 1923, 449A.

⁹⁷ *Ibid.*, E.P. 188,632; *J.*, 1923, 652A.

⁹⁸ *Ibid.*, G.P. 359,228; *J.*, 1923, 547A.

⁹⁹ C. Bennert, G.P. 361,038; *J.*, 1923, 264A.

¹⁰⁰ R. Haberer u. Co., G.P. 375,614; *J.*, 1923, 953A.

¹⁰¹ R. Haynn and F. Münz, Asers. to L. Cassella und Co., U.S.P. 1,451,299; *J.*, 1923, 547A.

¹⁰² E.P. 204,008; *J.*, 1923, 1173A.

¹⁰³ E.P. 174,595; *J.*, 1923, 141A.

¹⁰⁴ G.P. 867,090; *J.*, 1923, 398A.

¹⁰⁵ G.P. 371,231/3; *J.*, 1923, 767A.

¹⁰⁶ E.P. 189,046 and 189,054; *J.*, 1923, 52A.

¹⁰⁷ G.P. 365,785; *J.*, 1923, 398A.

¹⁰⁸ T. E. Rule, E.P. 200,375; *J.*, 1923, 827A.

Silk weighting, which is one of the most flagrant practices of adulteration permitted unchecked in connexion with an article of great value, is usually carried out by the dyer. Weighting with a vegetable syrup containing tannin, after dyeing, is proposed,¹⁰⁹ also weighting, before dyeing in the piece, with tin salts followed by a treatment with glycerin prior to weaving,¹¹⁰ and it has been patented also to apply salts of the rare earths, such as lanthanum ammonium nitrate, for the weighting of silk.¹¹¹

PRINTING.

Certain processes discussed under preceding sections have applications to printing, but in addition to these a number of improvements have been made of more or less special interest to the printer. According to P. Binder,¹¹² titanic oxide is superior to titanic acids for use in printing pastes, its covering power being superior to that of zinc oxide or barytes.

It is proposed to use chloroacetic acid or glycollic acid as dye solvent in printing pastes in place of acetic and formic acids as hitherto employed.¹¹³

An interesting patented process is one in which the leuco-derivatives of vat dyes are rendered soluble by conversion into salts of sulphuric acid esters, and in this form may be applied in dyeing and printing to yield fast shades after subsequent development on the fibre with oxidising agents.¹¹⁴ Another novel claim is to use the condensation product of formaldehyde and thiodiglycol in place of the usual oil mordants applied to the fixation of alizarin colours in dyeing and printing. Lake formation takes place with the new mordant only on steaming.¹¹⁵

The inability of zinc salts to react with potassium ferrocyanide in presence of ammonia is utilised by N. I. Planowski and K. S. Smirnov¹¹⁶ to make up printing pastes containing these reagents, along with a basic dye, which is fixed after printing, presumably by steaming to remove ammonia.

The intensity of shade of steamed Aniline Blacks is improved¹¹⁷ by adding an azo derivative of aniline, such as aminoazobenzene, to the padding or printing mixture, the amount of this addition permissible being not greater than one-fifth that of aniline. In connexion with Para Red and its homologues, C. and H. Sunder

¹⁰⁹ C. v. der Schmalz, U.S.P. 1,457,607; *J.*, 1923, 713A.

¹¹⁰ G. W. Cole, jun., U.S.P. 1,446,834; *J.*, 1923, 349A.

¹¹¹ Ges. f. Verwertung Chom. Prod. m. b. H., G.P. 373,771; *J.*, 1923, 971A.

¹¹² Bull. Soc. Ind. Mulhouse, 1923, 89, 196; *J.*, 1923, 651A.

¹¹³ J. R. Geigy, E.P. 183,813; *J.*, 1923, 972A.

¹¹⁴ Durand et Huguenin S.A., U.S.P. 1,448,251; *J.*, 1923, 398A.

¹¹⁵ Farbw. v. Meister, Lucius, und Brüning, G.P. 371,413; *J.*, 1923, 652A.

¹¹⁶ Bull. Inst. Polyt. Ivanovo-Voznesensk, 1923, 7, 115; *J.*, 1923, 826A.

¹¹⁷ G. Aris, E.P. 176,633; *J.*, 1923, 65A.

discuss the methods of diazotisation of *p*-nitraniline for use in dyeing and printing,¹¹⁸ while in connexion with discharge printing there is a further contribution from M. Battegay and P. Brandt, dealing with the rôle of anthraquinone as catalyst in formaldehyde-hydrosulphite discharges of Naphthylamine Claret.¹¹⁹ Half-resist effects on wool dyed with acid dyes are obtained after printing on Neradol D and steaming prior to dyeing, according to J. Pokorny.¹²⁰ M. Richard describes a process of khaki production on a naphthol prepare by printing with a paste containing vat dyes and iron pyrolignite,¹²¹ and R. Haller describes a process of obtaining Alizarin Red discharges on indigo-dyed cotton.¹²²

SIZING, FINISHING AND PROOFING.

Various chemical treatments allied to mercerisation, for the production of lustrous and other finishes, have been treated already in the section on mercerisation.

Sizing of yarn is not a finishing operation, but a treatment carried out primarily in aid of weaving, nevertheless it involves the use of finishing materials and is closely allied in practice to certain cloth-sizing treatments applied in connexion with finishing. Sizing of yarn is more or less important on all fibres in one or other connexion, but especially in the production of cotton goods, in order to attain smooth weaving uninterrupted by breakages of warp threads, and also regularity of weave. Such sizing is often made the vehicle for added weight, but this stale device has long been over-exploited, and a better opportunity for improving sizing is in the direction of applying a whole category of unsaponifiable fats, oils, and waxes, of which the chief is paraffin, which have hitherto been ruled out of use, or only surreptitiously employed, on account of the failure of aqueous scouring methods to remove them later when dyeing or bleaching is required. With the advent in bleaching of commercial solvent extraction the ban on the use of paraffin can be removed, if care is taken to ensure the goods having a suitable solvent treatment before bleaching.¹²³ The extension of the use of automatic looms, and the question of obtaining their greatly increased production, is largely dependent on adopting the most suitable sizing methods to allow of obtaining the increased speed in weaving, with a minimum of stoppages. The notable smooth-weaving properties imparted by soft paraffin should lead to a closer investigation of what can be done to improve sizing with materials of this kind, now the ban on their use is removable. Too much has been made of the difficulty

¹¹⁸ *Bull. Soc. Ind. Mulhouse*, 1923, **89**, 237; *J.*, 1923, 713A.

¹¹⁹ *Ibid.*, 1923, **89**, 365; *J.*, 1923, 1127A.

¹²⁰ *Ibid.*, 1923, **89**, 379; *J.*, 1923, 1127A.

¹²¹ *Ibid.*, 1923, **89**, 382; *J.*, 1923, 1127A.

¹²² *Ibid.*, 1923, **89**, 376; *J.*, 1923, 1127A.

¹²³ M. Fort, *J. Soc. Dyers and Col.*, 1922, **38**, 250.

of emulsifying unsaponifiable oils and waxes in the preparation of size; it can be accomplished usually with the aid of various well-known emulsifying agents, and with the aid of the colloid mill the most extreme cases should now present little difficulty.

A. E. Owen¹²⁴ has contributed an account of an investigation upon the effect of sizing on cotton yarns when under oscillatory tension, as in the loom, the upper limit of the safe range being well below the average breaking tension. Sizing greatly enhances the resistance to oscillatory strain, but the differences due to the variations in size mixing appear to be only small when compared with the differences due to variations in yarn structure. Increased resistance to oscillation, moreover, when conferred by sizing, is partly offset by the simultaneous imposition of a more limited capacity for ultimate extension without rupture.

A very important property of fibres, as it affects the finishing of textiles, is that of "plasticity," the property of taking a permanent set under strain, as opposed to so-called "elasticity." Operations like crabbing depend directly for attaining their purpose on a skilful use of this property of fibres, and great differences exist among the fibres, especially between the two great divisions of vegetable and animal fibres. An investigation by F. T. Peirce¹²⁵ into the plasticity of cotton is of interest, not because the results are directly applicable to finishing—the limited conditions, such as temperature, under which they were obtained prevent that—but on account of introduction of means of measuring plasticity and the new data being a first instalment which is capable of valuable extension.

A study of the flow of starch pastes through capillary tubes, with applications to viscometry applied to the testing of starch pastes, is contributed by F. D. Farrow and G. M. Lowe.¹²⁶ J. Huebner and V. Malwin¹²⁷ publish the results of tests of the effect on ripping strain and tensile strain of impregnating cotton with various salts, starch, and soap, and these allow it to be seen that a reduction in ripping strain does not involve a reduction in results obtained under tensile strain in all cases.

Papers on subjects of possible interest to certain special branches of textile finishing are one on synthetic resins by R. Furness,¹²⁸ and one dealing with the purification of commercial paraffin waxes by P. F. Gordon.¹²⁹

MISCELLANEOUS.

Micro-organisms play an important part in the retting methods applied for isolation of bast fibres, such as flax, from the stalk. In

¹²⁴ *J. Text. Inst.*, 1923, **14**, 375T.

¹²⁵ *Ibid.*, 1923, **14**, 391T.

¹²⁶ *Ibid.*, 1923, **14**, 414T; *Abstr.*, 1924, **B**, 50.

¹²⁷ *J.*, 1923, 66T.

¹²⁸ *Chem. and Ind.*, 1923, 1000.

¹²⁹ *J.*, 1923, 405T.

the course of an interesting discussion on the action of bacteria on cellulosic matter,¹³⁰ H. Langwell emphasised the error of the common assumption that chemically resistant cellulose is also resistant to bacterial action; on the contrary, it is destroyed by fermentation, which does not affect lignin. In the writer's opinion, the aromatic nucleus which is attributed to lignin, evidence of which he has observed in the course of special bleaching operations, may help to explain this resistance.

A paper on the distribution of iodine between chloroform and starch solution, by J. B. Frith and F. S. Watson,¹³¹ and one by G. T. Morgan¹³² on the new British dyestuffs industry may be noted.

The stream-line filter of H. S. Hele-Shaw¹³³ is of great interest on account of the possibilities it offers, such as clarifying peaty water, for separation and concentration of colloids, and its grading action on solutions, e.g., dyes.

Another imitation daylight lamp, of a not very novel type, has been patented,¹³⁴ and an apparatus for determining the melting point of coal ash is described by F. S. Sinnatt, A. B. Owles, and N. Simpson.¹³⁵

¹³⁰ *J.*, 1923, 279T (also 169T).

¹³¹ *J.*, 1923, 308T.

¹³² *Chem. and Ind.*, 1923, 868.

¹³³ *J.*, 1923, 353T.

¹³⁴ Gillet et Fils, E.P. 196,890; *J.*, 1923, 877A.

¹³⁵ *J.*, 1923, 266T.

ACIDS, ALKALIS, SALTS, ETC.

By H. J. BAILEY, O.B.E., F.I.C.

Inspector of Alkali etc. Works.

THE steady recovery in the heavy chemical industry experienced during the year 1922 was fairly well maintained during the early months of the year now under review. The stabilisation of prices and wages, which had been brought about after much anxiety and thought during the former year, has resulted in maintaining the progress already attained in the endeavour to recover from the severe depression of the year 1921. The production of sulphuric acid in this country was seriously influenced by the importation of large quantities of prepared superphosphate from the Continent, which during the season 1922-1923 reached a figure of about 100,000 tons, and it is feared may again reach similar proportions during the present season.

During the later months of the year the depression in the textile trades has reacted on the heavy chemical trades to some extent, and progress towards full recovery has been retarded.

In ammonia products the partial recovery of the steel industry, coupled with a brisk export trade for coke during the first half of the year, has brought the bulk of the by-product ovens of the country into commission, and resulted in larger production during 1923, all of which has been disposed of at fairly steady prices.

The production of sulphuric acid in the United Kingdom, as compared with that during the year 1922, has been estimated as follows :—

Sulphuric acid manufactured in the United Kingdom, expressed as tons of 100% H₂SO₄.

| | 1921. | 1922. | 1923 (estimate). |
|--------------------|---------|---------|---------------------|
| Chamber process .. | 533,000 | 773,000 | 807,000 |
| Contact process .. | 28,000 | 45,000 | 47,000 |
| Total | 561,000 | 818,000 | 854,000 |

Although the strenuous times through which industry has been passing do not lend themselves to the laying out of capital on new

industrial ventures, the past year has been quite fruitful in bringing to the fore certain new methods and processes which may have a very marked effect in shaping the industry of the future. Considerable progress has been made in investigations to utilise the remarkable absorbent properties of activated charcoal¹ and silica gel.² The former was found to be of great use for gas masks during the war, and since that time its application to the absorption of gases in peace-time industries has been carefully pursued; its more recent rival, silica gel, prepared by the precipitation of silica by means of acid from solutions of sodium silicate, is held by some to be a more efficient absorbent, but has this disadvantage in comparison with activated charcoal, that whereas the absorbed gases from charcoal can be driven out and the charcoal re-activated by the passage through it of superheated steam, the silica gel has to be furnace-d to drive off the absorbed products and to revivify the gel for the subsequent operation. E. M. Faber, H. G. Olson, and W. A. Taylor, have studied the absorbent properties of silica gel³ and its revivification at temperatures of 200° C., and find that for benzene, water, nitric acid, and nitrogen peroxide, complete recovery is obtained of the adsorbed substance with very little deterioration in efficiency of the gel for further absorptions. It is somewhat early to attempt to forecast in what directions the use of these solid absorbents may find application, but it is claimed that their effective use in benzol recovery has been proved, and further applications in the near future may be looked for.

The discovery of the "stream-line" filter⁴ by H. S. Hele-Shaw has opened up immense possibilities for the future in regard to filtration. When dealing with thin films of fluid the inventor found it possible not only to separate the finest particles of suspended matter, but also to separate fluids of different densities if the films were sufficiently attenuated. This led to further research, which resulted in the filter as known to-day consisting of packs of some thousands of thin sheets of material such as waterproof paper, which is not wetted by the material to be filtered. The packs of paper are held between press-heads on which the pressure necessary can be applied, and the papers are provided with similar perforations so that, when compressed, these perforations form tubes running from one end to the other of the pack. The liquid to be filtered is forced under great pressure into one or more of these tubes, passing in thin streams between the individual papers to the outlet tubes. The inlet or

¹ *Chem. and Ind.*, 1923, 850, 1141, 1164.

² *Ibid.*, 1923, 850, 1141, 1164.

³ *Chem. and Met. Eng.*, 1923, 28, 805; *J.*, 1923, 604A.

⁴ *J.*, 1923, 353T.

pressure tubes are made with larger perforations than the outlet tubes so as to provide the maximum space for the liquor to enter the minute interstices between the paper sheets. The material to be filtered from the liquor remains in the inlet tubes, and at definite intervals the flow is reversed and the sludge washed out. A filter containing 24 packs and approximately 34,000 sheets of paper can deal with $5\frac{1}{2}$ tons of liquor per hour, and the filter deals successfully with the finest of colloids, and apparently can remove substances such as certain colouring matters which were formerly held to be in solution and not merely in suspension. The application of this new method of filtration to various industries is being closely studied, and as a concentrator and as a filter there would appear to be numerous directions in which such applications would be of great utility.

The continued replacement of the Leblanc and ammonia-soda processes by electrolytic methods has led to the necessity of discovering wider fields for the application of the resultant chlorine. The experience gained during the past few years has made it possible to transport liquid chlorine with safety in cylinders and also in railway tank waggons, with the result that liquid chlorine is finding increasing outlets, the chief of which are for water purification and for the manufacture of bleaching liquors by absorption in alkalis at the works where such liquors are required. In addition there has sprung up a considerable industry in the manufacture of synthetic hydrochloric acid by burning the chlorine in excess of hydrogen and condensation of the product in water. In this way a product of high strength and considerable purity can be obtained, and production by this method is increasing in this and in other countries. During the early stages of the evolution of this process troubles were experienced due to explosions of the mixture of chlorine and hydrogen, and care must be taken to have an excess of hydrogen always present. The Badische Anilin- u. Soda-Fabrik⁵ avoids risk of explosions by arranging a continuously burning ignition flame at the place where the two gases are brought together. Discoloration of the resultant acid has also been a source of trouble, such discoloration frequently taking place some time after the acid has been manufactured and bottled. By some this discoloration was thought to be due to free chlorine, and B. Neumann⁶ considers that where free chlorine is found to exist in the acid it is due to faulty mixing or combustion, and not to any possible slight reversibility of the reaction $H_2 + Cl_2 = 2HCl$ at the high temperature of the reaction flame. In certain cases this trouble of discoloration has been overcome, and no doubt future experience will lead to the production of a

⁵ E.P. 173,300; J., 1923, 1130A.

⁶ Z. angew. Chem., 1923, 36, 529; J., 1923, 1173A.

perfectly colourless acid. G. Poma and G. Andreani⁷ produce synthetic hydrochloric acid by passing steam and chlorine over heated coke according to the equation $2\text{H}_2\text{O} + 2\text{Cl}_2 + \text{C} = 4\text{HCl} + \text{CO}_2$ and condensing the resultant hydrochloric acid with water in towers.

Little progress has been made during the year with the question of smoke and fume abatement. In the autumn session a Bill was introduced into Parliament with the object of increasing the penalties imposed under former Public Health Acts, and for giving powers to the Minister of Health to make orders for the extension of the Alkali &c. Works Regulation Act 1906, where such extension should be considered desirable, but the dissolution of Parliament has killed that particular measure.

Two new processes in connexion with the manufacture of sulphuric acid by the oxidation of the sulphur dioxide to trioxide by means of nitrous vitriol are attracting considerable attention. One, a process devised by K. B. Quinan, which is said to have been worked on a commercial scale at the works of the Cape Explosives Co. in South Africa, consists of Glover tower, converter, and two Gay-Lussac towers, without any large leaden chambers usually associated with the manufacture of vitriol by the nitration method. The Glover and Gay-Lussac towers function as in an ordinary chamber plant, but the whole of the sulphur dioxide which passes the Glover tower is converted into trioxide and condensed in the converter, which consists of a vertical cylinder fitted with a number of horizontal diaphragms perforated with a large number of small holes. Each diaphragm is provided with overflow pipes set at a suitable height, and the gases are forced by fan pressure sufficiently rapidly through the small perforations to maintain the seal on the diaphragms and a rapid ebullition of gas through the acid, producing intimate contact between the acid flowing down the tower and the sulphurous gases passing upwards. The converter is fed with nitrous vitriol of suitable strength,* and the principle involved appears to be very rapid conversion of SO_2 to SO_3 by means of intimate contact between ample supplies of nitrous vitriol and the gas. The converter is from 7 to 9 feet in diameter and 10 feet high for a production of over 40 tons of chamber acid per 24 hours. As far as the writer is aware this process has not been in operation outside the scope⁸ of the works under the supervision of the inventor, but the possibility of the rapid conversion of SO_2 to SO_3 by suitable intimate contact of the gas with nitrous vitriol is borne out by the success of the second process, that of T. Schmiedel.⁸ The Schmiedel or "splash-box" process is designed to effect rapid conversion of the sulphur dioxide

⁷ E.P. 189,723; J., 1923, 95A.

⁸ E.P. 187,016; J., 1922, 982A.

contained in the gases under treatment to 'sulphuric acid by rapidly circulating a large floating stock of nitrous vitriol through the apparatus, while bringing it into intimate contact with gases containing the sulphur dioxide. The unit consists of four or more splash-boxes, which are horizontal, rectangular, lead boxes provided with three rotating rollers each; the acid in these boxes is maintained at a constant level by suitable overflows, and the rollers rotate so as just to dip into the acid and produce a fine curtain of acid spray through which the gases bearing sulphur dioxide must penetrate in order to pass through the box. The gas inlets and outlets are at each end of the box and the rollers are placed at right angles to the flow of the gases. The plant can deal with cold gases of varying strengths and is easily adaptable for intermittent working. The first box acts as a denitrator for the acid, effecting some conversion of the sulphur gases as in a Glover tower; in the succeeding boxes the gases meet nitrous vitriol of suitable strength for rapid conversion of the remaining sulphur dioxide, the acid overflowing from the boxes is passed through coolers and back into circulation, the acid "make" being drawn off from the first or denitrating box. Following the last box is a spray catcher followed by absorption towers for recovery of oxides of nitrogen, which towers are lower, and of relatively greater sectional area than the usual type of Gay-Lussac tower. The first installation of this type of plant has been working for two years at Ausserfelden in Austria in connexion with copper matte converters belonging to the Mitterberger Kupfer A.G., Salzburg, and has been dealing with gases varying in sulphur dioxide content from 0 to 15% with production varying between 6 to 10 tons of 142° Tw. acid per day, according to the sulphur material available. Through the kindness of Messrs. Huntington, Heberlein & Co. it is possible to state that licenses for the erection of this type of plant have now been granted to firms operating in England, Australia, France, Germany, Austria, Spain, and Japan; the licence granted in England is in connexion with the calcination of zinc blende, and results will doubtless be followed with very great interest.

The nitration process for the manufacture of sulphuric acid is of such long standing that it might almost be concluded that all was known that could be discovered, yet the modern progress of first the Opl tower plant, then the reduction of chamber capacity by the Mills-Packard system of chambers, and latterly these two new methods, has shown that the rate of conversion of the sulphur dioxide to trioxide can be enormously speeded up by circulating sufficient acid to carry the nitre stocks necessary for conversion, and by bringing such nitrous acid into intimate contact with the gas.

HAFNIUM.⁹

The discovery of a new element to fill up one of the few remaining gaps in the periodic table of elements was announced by D. Coster and G. Hevesy in the early part of the year. This element was named hafnium and filled the space belonging to the atomic number 72, a space formerly claimed by Urbain and Dauvillier for a rare earth element called celtium. Coster and Hevesy isolated the new element from zirconium and found that it occurred in appreciable quantities in all the zirconium minerals they examined. Considerable discussion has taken place in technical literature as to the claims of priority of discovery, and as to whether the name finally accorded to the element 72 shall be hafnium or celtium—a matter which the International Committee on the elements will have to decide.

GEORG LUNGE.¹⁰

The death of Georg Lunge on January 3rd, 1923, at the age of 84, removed one whose name has been closely associated with acids and alkalis for over half a century. His association with industrial chemistry and his classical text-book on the subject have made his name of world-wide repute. The first edition of his "Sulphuric Acid and Alkali" appeared in 1879; this was revised and extended in subsequent editions, until, with the companion volumes on "Coal Tar and Ammonia" it extended to nine volumes. Many of the processes described in the earlier editions of his book have now become extinct, and it is a somewhat singular coincidence that in the year of his death there should appear an entirely new edition of his work revised and brought up to date, which edition is being produced under the editorship of A. C. Cumming.¹¹ The volumes of this edition are arranged so as to deal with the subjects treated in relation to separate branches of industry, and from perusal of the three volumes already published will maintain and, if possible, add to the value of the work.

SIR JAMES DEWAR.¹²

The death at the age of 80 of Sir James Dewar removed another scientific pillar of the last generation, and one whose name will always be associated with scientific progress of the last half century, more especially in relation to liquefaction of air and other gases.

⁹ *Chem. and Ind.*, 1923, 67, 258, 764, 784, 884, 929.

¹⁰ *Ibid.*, 1923, 78.

¹¹ *Ibid.*, 1923, 702, 1217; *Analyst*, 1923, 516.

¹² *Ibid.*, 1923, 326, 344.

THE UNITED ALKALI COMPANY.¹³

The centenary was celebrated this year of the founding of the beginnings of this Company. James Muspratt commenced operations in Liverpool and worked the Leblanc soda process in 1823, and this historic event has caused many to look back and review how the alkali industry has grown during the past century. One might almost say that the industrial life of this country has grown out of the foundations of the heavy chemical industry. The event was marked by a dinner given by the Company at Liverpool, on April 18th, when a large number gathered to offer their congratulations. The formation of the Company as known to-day took place in 1890, when a number of firms operating the Leblanc process amalgamated at a time when the menace of the competition of the ammonia-soda process, and of the electrolytic process for the production of caustic soda, made it necessary to work the older process as economically and efficiently as possible.

BRUNNER, MOND, AND CO.¹⁴

This year has also seen the celebration of the jubilee of the above company, the founders of the ammonia-soda process for alkali manufacture in this country. The ammonia-soda process has now quite replaced the Leblanc process for the manufacture of soda-ash, and is in its turn finding a serious rival in the electrolytic process of treating brine.

FIXATION OF NITROGEN.

Progress has been continued in the construction of the new plant of Synthetic Ammonia and Nitrates, Ltd., at Billingham, and it is hoped that at an early date the production stage will be reached. This plant has been erected after agreement with the Government to manufacture nitrogen products from the air on the lines of the Haber process. In the first instance, the main product will be ammonium sulphate, but later on it is expected that other nitrogen products will be produced.

The British Cyanides Co., Oldbury, is just completing the installation of the first unit for the fixation of nitrogen in the form of cyanide, which, if successful, will be rapidly followed up by additional units.

In France the position of the nitrogen industry has been engaging serious attention during the year.¹⁵ Production still remains round about 19,000 tons of nitrogen per annum, whereas agricultural consumption alone has increased to roughly 110,000 tons.

¹³ *Chem. and Ind.*, 1923, 27, 383, 393, 415, 487.

¹⁴ *Ibid.*, 1923, 675.

¹⁵ *Ibid.*, 1923, 228, 501.

Agreements have been concluded with the Badische Anilin und Soda Fabrik to work the Haber process and to produce by this method up to 100 metric tons of fixed nitrogen per day. The Claude process at Montereau is now producing 5 tons of ammonia per day, and at Bethune a large plant has been installed to utilise the gases from the coke-ovens there, while the Cie. des Produits Chimique d'Alais is installing plant to exploit the Casale process, which has been favourably reported upon by the Director of the Service des Poudres.

In Spain,¹⁶ at Flix (Tarragona), a factory is being erected to produce 1000 kg. of ammonia daily by the Claude process, the hydrogen to be derived from an adjacent electrolytic soda plant.

Various improvements have taken place during the year in the several processes, but these have been mainly in working details, and no radical change has taken place. G. Claude¹⁷ patents the preliminary heating of the reaction gases up to the reaction temperature. K. P. McElroy¹⁸ patents a method of fixation as cyanide, by arranging to draw off a portion of the hot gases from the reaction blast furnace near the fusion zone, and bringing these gases carrying cyanide vapour in contact with alkali and carbon in the presence of highly absorptive charcoal at a high temperature; molten cyanide is maintained in the bottom of the furnace and run off from time to time as it accumulates.

F. C. Dyche-Teague, A. Wilson-Hughes, and F. J. Commin¹⁹ produce a reactive mass for the production of cyanide, by mixing carbon, soda ash, and iron oxide, and treating the mixture with an oil emulsified with sodium rosinate. The product is dried and granulated and then passed through a furnace at 900°–1050° C. in a current of nitrogen. The reactive mass is occasionally treated with superheated steam, which tends to make it more active, and it is found that a small percentage of hydrogen in the nitrogen increases the amount of alkali converted into cyanide. W. Steger²⁰ adds further supplies of reaction mixture direct into the reaction zone of the blast furnace through the blast inlets.

B. Waeser²¹ has published a treatise on the nitrogen industry, as also have J. R. Partington and L. H. Parker.²² These works bring into text-book form much that was formerly only available after search amongst specifications of patents and technical papers, and in the latter book extensive use is made of the Nitrogen

¹⁶ *Chem. and Ind.*, 1923, 524, 752.

¹⁷ E.P. 171,972; *J.*, 1923, 54A.

¹⁸ E.P. 191,765; *J.*, 1923, 352A.

¹⁹ E.P. 192,791; *J.*, 1923, 353A.

²⁰ G.P. 364,589; *J.*, 1923, 353A.

²¹ *Chem. and Ind.*, 1923, 435.

²² *Ibid.*, 1923, 435.

Products Committee Report. E. Kilburn Scott²³ in the Cantor lectures before the Royal Society of Arts gave a valuable *résumé* of nitrogen fixation methods and explained "in detail the Kilburn Scott and Nitrum arc furnaces.

The process devised by G. Fausser²⁴ has recently been applied on an industrial scale at Novara in Italy. This process is for the production of synthetic ammonia and somewhat resembles the Haber process. The hydrogen is produced by electrolysis in cells specially designed to avoid danger of explosion. The mixed gases are passed over the catalyst at a pressure of 300 atmospheres, and any ammonia not liquefied is absorbed in water, this aqueous solution being used to lubricate the compressor. An oxidation plant of Frank and Caro, yielding 10 tons of nitric acid per day, is attached, and the residual gases from this plant containing little oxygen and much nitrogen are burnt with the necessary quantity of hydrogen, by means of platinised asbestos, so as to remove the oxygen as water, and produce an almost pure nitrogen gas for use in the main synthetic plant. This method of producing nitrogen would appear to be well worthy of consideration at other plants where the main output required is nitric acid or nitrates.

AMMONIUM COMPOUNDS.

R. A. Mott and H. J. Hodson²⁵ published results of work done on the dissociation of ammonia in the presence of coal gas, and also the influence of water vapour and various contact materials at high temperatures. In a previous communication²⁶ possible oxidation of ammonia in crude coal gas by indrawn air was considered to be negligible, as preferential combination of the hydrogen present with such oxygen took place, and in presence of air oxidation of ammonia was retarded by the presence of water vapour. The experiments were only conducted up to temperatures of about 800° C., while these later experiments have been taken to higher ranges. Generally the results obtained confirmed the work of G. E. Foxwell,²⁷ except that the authors find that the velocity of decomposition increases fairly rapidly with rise of temperature. Firebrick material "chattered" by the action of salt vapours in a coke oven proved an active catalyst, and the catalytic activity of brick material was found to depend on the proportion and condition of the iron present.

Further progress has been made and experience gained in the production of neutral, dry ammonium sulphate. This product

²³ *Chem. and Ind.*, 1923, 498.

²⁴ *Ibid.*, 1923, 835; A. Zambianchi, *Giorn. Chim. Ind. Appl.*, 1923, 5, 171; *J.*, 1923, 601A.

²⁵ *J.*, 1923, 4T, 26T, 39T.

²⁶ *J.*, 1922, 273T.

²⁷ *J.*, 1922, 114T.

has now established itself as the permanent high-grade commercial article, and, in spite of minor difficulties of dust and caking in certain instances, has generally given satisfaction and has assisted in maintaining a brisk export trade in this commodity during the year.

G. Royston²⁸ patents a method of neutralising the wet sulphate, after having been discharged from the saturator, in a closed lead box, by injecting ammonia - pours drawn from the still gases through the wet salt. The process is good from the point of view of neutralisation, but does not provide for drying the salt after centrifuging, and neutralisation of much mother liquor must take place along with the salt. Also, as worked so far, the escape of steam may be objectionable in carrying off into the atmosphere impurities associated with the ammonia in the still gases, and possibly excess of ammonia which may be lost. The variation in the pressure of the saturator, when such still gases are being drawn off to the neutraliser, may also lead to rock salt troubles.

R. P. Douglas²⁹ utilises the still gases for neutralising the wet sulphate, but first cools and purifies the ammonia by passage through a condenser and purifier.

G. A. Phillipson³⁰ dries and neutralises the crude salt in a vertical cylindrical apparatus provided with hollow trays and rotating scrapers which pass the salt from one tray to another, steam or hot air being supplied to the hollow portion of the trays, and ammonia with hot air or other gas being passed through the cylinder.

A. H. Thwaite and Pease and Partners, Ltd.,³¹ treat the moist acid salt in a steam-jacketed drying cylinder provided with an Archimedean screw mounted on a hollow shaft having perforations, through which the neutralising ammonia gases flow, and come in direct contact with the salt.

G. Weyman³² claims that the neutral salt after leaving the centrifugal can be dried without application of external heat if efficient contact with air while the salt is hot is provided for. The salt is elevated and dropped over a screen, from which it falls in a fine shower into light heaps on the store-room floor. The screen may be mechanically agitated and provided with crushing devices for breaking up lumps.

T. Lewis Bailey³³ gives further consideration to the working conditions in regard to extraction of phenols from the effluent

²⁸ E.P. 188,587; J., 1923, 54A.

²⁹ E.P. 194,625; J., 1923, 400A.

³⁰ E.P. 196,115; J., 1923, 549A.

³¹ E.P. 203,013; J., 1923, 1069A.

³² E.P. 205,301; J., 1923, 1222A.

³³ 59th Rept. of Chief Inspector of Alkali, etc., Works, 1922; J., 1923, 885A; Chem. and Ind., 1923, 990.

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²³ *Chem. and Ind.*, 1923, 498.

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²⁵ *J.*, 1923, 4T, 26T, 39T.

²⁶ *J.*, 1922, 273T.

²⁷ *J.*, 1922, 114T.

H. W. Webb and M. Taylor³⁷ have examined the accuracy of the nitrometer method for determination of nitrogen in nitrates and nitric acid, and found that when 91-92% sulphuric acid is employed the correction of 0.35 c.c. of nitric oxide per 10 c.c. of sulphuric acid, as given by Lunge, is too high, and should be only 0.20 c.c. They also found that, with reasonable care as to loss of fume etc., nitrometer tests were fairly accurate both with nitric acid and nitrates.

H. W. Webb³⁸ has published a book on the "Absorption of Nitrous Gases," which has collected together in text-book form much of the research and experience gained at the Government Factories.

P. Pascal and Garnier³⁹ have investigated the properties of mixtures of nitric and sulphuric acids in relation to specific gravity, specific heat, and distillation, and their action on aluminium, steel, and lead, and have recorded data which should be extremely useful to the chemist dealing with the manufacture of explosives.

BORIC ACID.

The production of boric acid from volcanic steam in Tuscany⁴⁰ has opened up a further source of supply of this commodity. The steam is tapped by means of bore-holes and issues at temperatures of 120°-130° C. It is then condensed in boilers which generate steam for the production of electricity supplied to neighbouring towns. The condensed natural steam is evaporated in shallow lead-lined troughs by means of the partially exhausted steam, and from the concentrated liquors crude boric acid is deposited. The industry is still in its infancy, but an output of 10 tons a day of boric acid has been reached at the works at Castelnuovo.

HYDROGEN ION CONCENTRATION.

The modern method of investigation of dilute solutions by determining the hydrogen ion concentration has received further attention, and methods have been worked out for titration of salts which ionise in solution with electrometric control. J. W. Shipley and I. R. McHaffie⁴¹ have determined the limits of hydrogen ion concentration in relation to carbon dioxide, calcium carbonate, and calcium sulphate. The same authors⁴² have also determined the solubility and hydrolysis for saturated solutions of calcium carbonate. W. Mansfield Clark⁴³ has published a

³⁷ *J.*, 1922, 362T.

³⁸ *Chem. and Ind.*, 1923, 719.

³⁹ *Mém. Poudres*, 1923, 20, 39; *J.*, 1923, 652A.

⁴⁰ *Chem. and Ind.*, 1923, 1022.

⁴¹ *J.*, 1923, 311T.

⁴² *J.*, 1923, 319T, 321T.

⁴³ *Chem. and Ind.*, 1923, 1042.

second edition of a text-book on determination of hydrogen ions. The study of the hydrolysis of dilute solutions is coming more and more into prominence, and questions such as the corrosion of iron and the suitability or otherwise of certain water supplies for industrial purposes are being dealt with along these lines.

HYDROGEN PEROXIDE.

The extension of the use of hydrogen peroxide in the bleaching of textile and other products is dealt with by J. E. Weber,⁴⁴ who gives evidence that in certain cases this method of bleaching is becoming an economic proposition, especially in such cases where the ordinary hypochlorite method might endanger the fabric⁴⁵.

LIQUID AIR.

This article is becoming of rapidly increasing importance in connexion with the fixation of nitrogen, in addition to being the main source of the oxygen now so largely in use in many directions. E. Fyleman⁴⁶ gave a valuable paper on the explosions which have occurred in liquid air rectification plant; these explosions have been at times of a very serious nature, involving loss of life. The paper set forth the results of an investigation into the cause of these troubles and created a very useful discussion of the problem. It was found that the chief cause of the trouble was acetylene, which was formed by the action of the compressed air on the lubricating oil of the air-compressor; the acetylene was so stable at the temperature of the liquid oxygen bath that it accumulated there. The action on the lubricating oil was found to take place at fairly high temperatures, so that the keeping of valves and other portions of the compressors cool, and employing suitable lubricating oil of high flash-point, and the banning of carbide in any form from the neighbourhood of the plant proved to be a sufficient safeguard against the occurrence of such explosions. A. E. Malpas⁴⁶ referred to the adoption of the precaution of running off a small portion of the liquid oxygen every hour from the receiver where the solid acetylene was trapped; in this way in the Norwegian plants the accumulation of acetylene was avoided and all risk of explosion done away with.

MAGNESIUM CHLORIDE.

P. Cottringer and W. R. Collins⁴⁷ produce anhydrous magnesium chloride by heating the dry powdered oxide in a current of

⁴⁴ *Chem. Tr. J.*, 1923, 515.

⁴⁵ *J.*, 1923, 37T, 152, 127, 139T.

⁴⁶ *J.*, 1923, 142T.

⁴⁷ U.S.P. 1,450,912; *J.*, 1923, 657A.

dry hydrogen chloride gas at a temperature of 430°-550° C., any excess of hydrochloric acid gas being dried with concentrated sulphuric acid and used over again. O. H. Weber and P. Siedler⁴⁸ heat mixtures of ammonium chloride and hydrated magnesium chloride to produce anhydrous magnesium chloride. B. S. Kirkpatrick and F. S. Morgan⁴⁹ propose to produce anhydrous metallic chlorides by acting upon a suitable alloy of the metal with chlorine gas, the alloy being in a molten state.

OZONE.

F. E. Hartman,⁵⁰ in the course of a valuable *résumé* of the present position of the industrial application of ozone, describes the methods of manufacture in ozonisers of the non-dielectric and dielectric types. Experimental data are given of the action of ozonised air in accelerating the drying of varnishes, the bleaching of oils, and in the oxidation and drying of linseed oil. The use of ozone in the preparation and preservation of foodstuffs and in the prevention of moulds is referred to, and indications are given of the possibility of the many and varied industries to which it can be applied.

POTASSIUM AND SODIUM SALTS.

That the world's future requirements of potash are well assured for some hundreds of years appears to be the outcome of the year's progress in regard to this important commodity. The output of potash from Alsace⁵¹ reached the enormous figure of 1,326,727 tons in 1922, as compared with 903,134 tons in 1921, 1,222,370 tons in 1920, and 592,365 tons in 1919. In Czechoslovakia⁵² large deposits of potash have been discovered, estimated to contain millions of tons. In Italy⁵³ methods have been worked out for bringing into commercial utility the potash contained in leucite, a mineral occurring in very large quantities among the lavas of the Italian volcanoes. The development of the potash industry from leucite has been due to Baron Blanc, who, after overcoming considerable opposition and difficulties, has brought the processes to a state of commercial utility. The pure mineral contains 21.5% of potash in the form of a double silicate of potassium and aluminium, and it is calculated that over the whole range of the Italian volcanoes the leucitic lavas contain at least 8,786,000,000 metric tons of potash, making them the greatest

⁴⁸ G.P. 371,143; *J.*, 1923, 719A.

⁴⁹ U.S.P. 1,455,005; *J.*, 1923, 657A.

⁵⁰ *J.*, 1923, 117T.

⁵¹ *Chem. and Ind.*, 1923, 523.

⁵² *Ibid.*, 1923, 1061.

⁵³ *Ibid.*, 1923, 1125, 1133.

accumulation of potash silica rocks known. Three methods have been worked out for recovery of the potash; in each case the mineral after mining is crushed to a convenient size. In the first process the mineral is treated with sulphuric acid, which dissolves out the potash and alumina, producing a potash alum. In the second method the bed of crushed leucite is treated with chloride mother liquors and hydrochloric acid gas, which dissolves out the potash and alumina as mixed chlorides; the potassium chloride is crystallised out on cooling, while hydrated aluminium chloride is thrown down by further treatment of the cold liquor with hydrochloric acid gas, the residual mother liquor being used again for further treatment of leucite. The third method consists in treating the leucite with slaked lime in autoclaves for three hours at pressures of about 200 lb. to the square inch; the liquid produced is used in the similar treatment of further batches of leucite until ultimately a 12% solution of caustic potash is obtained. The residue from the autoclaves has been found to make an excellent cement.

When one looks back to the serious difficulties experienced by the Allies during the Great War in obtaining adequate supplies of potash materials, these huge supplies now available, at present-day commercial prices, are yet another indication of the magician's wand which the chemical industry has so often wielded for the good of mankind.

The British Cyanides Co. is now manufacturing potassium permanganate by electrolysis, a new industry for this country.

J. W. Turrentine, H. G. Tanner, and P. S. Shoaff^{53a} describe a method of producing potassium chloride from kelp brine, with recovery of iodine, and of sodium chloride of sufficient purity for table use.

M. M. Green⁵⁴ gives a method of determination of potassium in acid-insoluble silicates, which depends on the assumption that all metals except potassium form perchlorates soluble in 97% alcohol. The method requires only 2-3 hours, and is said to be reliable to $\pm 0.2\%$.

R. Hubert⁵⁵ discusses the various methods of determining potash and describes a method of Przibylla in which the solution is shaken with an excess of sodium bitartrate solution, at a maintained temperature of 18° C.; the mixture is then filtered, and the filtered solution titrated either with N/10 sodium carbonate, or with N/10 sodium hydroxide, using rosolic acid as indicator. The potassium content is then read off from tables or curves

⁵³ J., 1923, 15, 159; J., 1923, 306A.

⁵⁴ J., 1923, 15, 153; J., 1923, 307A.

⁵⁵ U.S.P. 1,414, Mulhouse, 1922, 88, 500; Ann. Chim. Analyt., 1923, 2A, 181A.

constructed from results obtained from standard preparations. This latter method is said to take 40 minutes and to be accurate to 0·3% K₂O.

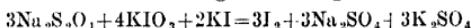
A new process for the manufacture of sodium thiosulphate has been described by L. Hargreaves and A. C. Dunningham.⁵⁶ The process consists in producing the reaction between sodium sulphite and sulphur at such concentrations that the interaction is rapidly increased, and a concentrated solution of the thiosulphate formed in which any excess of sodium sulphite is practically insoluble. It was found that this could be done in a digester provided with a mechanical agitator, into which solid sulphite and sulphur are introduced along with the requisite quantity of water. The addition of further quantities of the solid reagents are made from time to time, and the concentrated solution of thiosulphate is drawn off through heated vacuum filters and receivers, and passed to crystallisers from whence the mother liquor is returned to the digester. In this way costs of evaporation of bulky solutions are eliminated and a considerable output is obtained from a plant of comparatively small size. When supplies of cheap sulphite were not available the authors found that by treating sodium carbonate and sulphur in a preliminary tower with sulphur dioxide, and running the product into the digester, an equally satisfactory process could be worked out on similar lines. Frothing troubles which were expected, due to the evolution of the carbon dioxide, were overcome by means of a special form of froth destroyer interposed between the tower and digester. The process seems to be distinctly good and should prove to be economical in working and easily elastic as to output.

R. W. Merriman⁵⁷ has pointed out that sodium hydrosulphite (Na₂S₂O₄) is coming more and more into use in industrial processes. In addition to its use in vat dyeing it may be used for the determination of oxygen in gases, the removal of oxygen from gases for technical purposes, determination of nitro-compounds and dyestuffs, the manufacture of dyestuffs, intermediate products, and drugs, and the bleaching of a variety of materials. It has become increasingly necessary to discover a convenient and reliable method of determining the hydrosulphide value of a given sample; the indigo-carmine method is suitable for vat dyers who require to examine the material every day, but the apparatus required is complicated and a supply of 100% indigo must be available. The author describes a method of analysis dependent upon the action of iodine on the products formed when sodium hydrosulphite is dissolved in a solution containing excess of formaldehyde. Iodine is added in excess and titrated

⁵⁶ J., 1923, 147T.

⁵⁷ Chem. and Ind., 1923, 290.

back with standard sodium thiosulphate solution, using starch as an indicator. Messrs. Brotherton and Co., Ltd.,⁵⁸ have published a method for determining sodium hydrosulphite which is dependent upon the reaction occurring with mixtures of potassium iodate and potassium iodide according to the equation :—



Excess of thiosulphate is added and titration effected with standard N/10 iodine solution. Both these processes are unaffected by admission of oxygen, and with reasonable experimental care should prove useful and reliable methods.

J. B. Firth and J. Higson⁵⁹ have investigated the action of sodium hydrosulphite on silver chloride, both in the solid state and dissolved in thiosulphate solution, and in ammoniacal solution. When the silver chloride is dissolved in thiosulphate a theoretical recovery of the silver is effected as sulphide, when in ammonia as metallic silver, and it is suggested that recovery of silver from silver chloride residues might be conveniently effected by these means.

P. Pascal and Ero⁶⁰ have studied the solubility and melting points of mixtures of sodium sulphate and sulphuric acid, and have investigated the possibilities of recovering the acid from such mixtures by refrigeration or by deposition of the mixed sulphates from more concentrated solutions.

SULPHUR AND SULPHURIC ACID.

In the report for last year attention was drawn to the fact that sulphur as a raw material for the manufacture of sulphuric acid had almost replaced imported pyrites in America, and that in other countries the use of sulphur in place of pyrites was purely an economic question. In the early part of this year an agreement was made between the producers of sulphur in Italy and America⁶¹ which fixed prices and allocated markets so that the industry in both areas should be maintained, and the world's requirements of sulphur be met without either interest being killed. The Frasch process had given the American producer such an enormous advantage in cost of production, from supplies which appear to be inexhaustible, that there had been a serious danger of the Sicilian industry being abandoned, and although one always has the fear that combines of producers may militate against the buyer, yet the maintenance of the sulphur industry in both parts of the world should in the end be to the advantage of the consumer. During

⁵⁸ *Chem. and Ind.*, 1923, 1131.

⁵⁹ *J.*, 1923, 427T.

⁶⁰ *Mém. Poudres*, 1923, 20, 1; *J.*, 1923, 653A.

⁶¹ *Chem. and Ind.*, 1923, 375.

the year a further increase in the consumption of sulphur as a raw material for acid manufacture in the United Kingdom has to be recorded, and the appended table sets out the approximate amounts of pyrites, spent oxide, and sulphur so consumed :—

*Raw materials consumed for acid manufacture in Great Britain and Ireland.
Long tons.*

| Year | Pyrites. | Spent oxide. | Sulphur. |
|--------------------|----------|--------------|----------|
| 1920 | 686,000 | 139,000 | 5,000 |
| 1921 | 313,900 | 103,000 | 8,000 |
| 1922 | 391,000 | 157,000 | 30,000 |
| 1923 (estimate) .. | 348,000 | 145,000 | 66,000 |

During the past year rather more acid has been made from the gases given off in the calcination of zinc blende in Great Britain, and it is estimated that acid so produced during 1923 will represent some 27,000–28,000 tons as 100% acid, as compared with 17,000–18,000 tons during 1922. Such increased output has all been obtained from plant formerly in existence, and no real development has occurred during the year ; arrangements are, however, being made for starting up calciners in connexion with the former Government plant at Avonmouth, so that possibly the year 1924 may see important developments in this direction.

The advent of some simple and inexpensive process for the conversion of these spelter gases into acid would alter the whole complexion of the problem, and it is possible that a process, such as that of Schmiedel, described earlier, may alter the whole position of acid manufacture in this country.

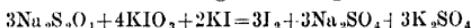
C. Opl⁶² has described a modification of the tower system of acid manufacture in which the nitration of the sulphur gases takes place in iron vessels half filled with nitrous vitriol. There are six of such vessels placed in series ; depitration takes place in the first of these and nitration in the remaining five, the residual gases being passed through a coke-packed tower. The sulphur gases are cooled and forced through the reaction vessels, and it is stated that results are comparable with those obtained in the original tower system.

H. Petersen⁶³ suggests passing gases bearing sulphur dioxide through a series of lead boxes packed with broken quartz through which nitrous vitriol is passed on the counter-current principle. Both these suggestions appear to have insufficient provision for the necessary time contact to effect complete nitration of the sulphur dioxide gases along with simultaneous revivification of

⁶² *Chem.-Zeit.*, 1923, 47, 485 ; *J.*, 1923, 713A.

⁶³ *Ibid.*, 1923, 47, 227 ; *J.*, 1923, 398A.

back with standard sodium thiosulphate solution, using starch as an indicator. Messrs. Brotherton and Co., Ltd.,⁵⁸ have published a method for determining sodium hydrosulphite which is dependent upon the reaction occurring with mixtures of potassium iodate and potassium iodide according to the equation :—



Excess of thiosulphate is added and titration effected with standard N/10 iodine solution. Both these processes are unaffected by admission of oxygen, and with reasonable experimental care should prove useful and reliable methods.

J. B. Firth and J. Higson⁵⁹ have investigated the action of sodium hydrosulphite on silver chloride, both in the solid state and dissolved in thiosulphate solution, and in ammoniacal solution. When the silver chloride is dissolved in thiosulphate a theoretical recovery of the silver is effected as sulphide, when in ammonia as metallic silver, and it is suggested that recovery of silver from silver chloride residues might be conveniently effected by these means.

P. Pascal and Ero⁶⁰ have studied the solubility and melting points of mixtures of sodium sulphate and sulphuric acid, and have investigated the possibilities of recovering the acid from such mixtures by refrigeration or by deposition of the mixed sulphates from more concentrated solutions.

SULPHUR AND SULPHURIC ACID.

In the report for last year attention was drawn to the fact that sulphur as a raw material for the manufacture of sulphuric acid had almost replaced imported pyrites in America, and that in other countries the use of sulphur in place of pyrites was purely an economic question. In the early part of this year an agreement was made between the producers of sulphur in Italy and America⁶¹ which fixed prices and allocated markets so that the industry in both areas should be maintained, and the world's requirements of sulphur be met without either interest being killed. The Frasch process had given the American producer such an enormous advantage in cost of production, from supplies which appear to be inexhaustible, that there had been a serious danger of the Sicilian industry being abandoned, and although one always has the fear that combines of producers may militate against the buyer, yet the maintenance of the sulphur industry in both parts of the world should in the end be to the advantage of the consumer. During

⁵⁸ *Chem. and Ind.*, 1923, 1131.

⁵⁹ *J.*, 1923, 427T.

⁶⁰ *Mém. Poudres*, 1923, 20, 1; *J.*, 1923, 653A.

⁶¹ *Chem. and Ind.*, 1923, 375.

to be of such a small size that they adhere to the surface of the cleaned plate, thus forming a protective coating against further corrosion by the acid.

J. M. Taylor⁷⁰ gave a useful paper on the determination of sulphur in pyrites and in certain other sulphur compounds; discrepancies in results in sulphur determinations are always liable to occur in the hands of different operators, and the more the methods adopted can be standardised the less will be the likelihood of such disagreements.

Rex Furness⁷¹ has reviewed the preferential oxidation of hydrogen sulphide in the presence of catalysts, including the purification of fuel gases with activated charcoal at ordinary air temperatures, and the hot purification method as adopted in the Claus kiln. With activated charcoal the sulphur formed is recovered by suitable solvents such as carbon disulphide, but so far it is doubtful if the process can economically replace the iron oxide method of purification. That there was considerable scope for further progress on these lines was indicated, as methods for direct recovery of the sulphur by suitable catalysts might be both economical in operation and possibly profitable.

In certain cases the reverse reaction, namely the reduction of sulphur dioxide to hydrogen sulphide or sulphur, would be extremely useful, especially if this could be done with gases in which the sulphur dioxide content was variable or low. Some investigations have been carried out on this interesting problem.

M. G. Tomkinson⁷² reduces sulphur dioxide by passing the gas mixed with hydrogen over finely divided nickel or nickel sulphide at 400°–450° C. B. C. Stuer⁷³ passes sulphur dioxide along with a reducing gas over hydrated iron oxide, or hydrated oxides of chromium or aluminium and also hydrated silica. B. Rassow and K. Hoffmann⁷⁴ have investigated the production of carbon disulphide from sulphur dioxide and heated charcoal. So far there is no information that any of these attempts has met with practical success.

P. W. Edwards⁷⁵ describes explosion troubles in the preparation of finely divided sulphur for use as an insecticide. The sulphur is prepared by spraying polysulphide solution into hot furnace gases, and collecting the fine sulphur in bag filters. It was found that a high electrostatic charge accumulated on the bags which probably gave rise to the fires and explosions, and earthing of the bags with a material such as aluminium, brass, lead, or steel is recommended.

⁷⁰ *J.*, 1923, 294T.

⁷¹ *Chem. and Ind.*, 1923, 196.

⁷² *Comptes rend.*, 1923, 176, 35; *J.*, 1923, 142A.

⁷³ G.P. 305,621; *J.*, 1923, 224A.

⁷⁴ *J. prakt. Chem.*, 1923, 104, 207; *J.*, 1923, 207A.

⁷⁵ *Chem. and Met. Eng.*, 1922, 27, 986; *J.*, 1923, 53A.

ZIRCONIUM.

The industrial application of the oxide of this metal has attracted further attention, and various methods have been suggested for preparation of the oxide from the mineral. H. von Siemens and H. Zander⁷⁶ prepare pure oxide by passing a stream of chlorine over a mixture of Brazilian zirconia with 25% of charcoal heated to a temperature above 1000° C.; crystalline $ZrOCl_2$ is obtained, which is further purified and then ignited in air to produce pure oxide. F. G. Jackson and L. I. Shaw⁷⁷ fuse zirconia with a mixture of borax and sodium carbonate, dissolve the metals as chlorides, and then treat the dissolved chlorides with sulphuric acid to obtain the basic sulphate of zirconium and titanium. This process is said to be slow and tedious but efficient for removing iron, alumina, and silica. J. W. Bain and G. E. Gollop⁷⁸ digest zirkite with concentrated sulphuric acid and dilute the extract with water. The solution of basic sulphate is treated with calcium carbonate or chloride, and the calcium sulphate filtered off, the filtrate considerably diluted, and the precipitate filtered, washed and ignited. L. E. Barton and C. J. Kinzie⁷⁹ heat the mineral with an alkali bisulphate, the resultant product being lixiviated. O. Ruff⁸⁰ heats the ore with the requisite quantity of an alkali carbonate, the insoluble zirconium compounds thus produced being dissolved in acid.

⁷⁶ *Wiss. Veröffentl. Siemens-Konzern*, 1922, **2**, 484; *J.*, 1923, 143A.

⁷⁷ *J. Amer. Chem. Soc.*, 1922, **44**, 2712; *J.*, 1923, 182A.

⁷⁸ *Canad. Chem. and Met.*, 1923, **7**, 35; *J.*, 1923, 351A.

⁷⁹ U.S.P. 1,451,004; *J.*, 1923, 549A.

⁸⁰ U.S.P. 1,454,564; *J.*, 1923, 718A.

GLASS.

By E. A. COAD-PRYOR,

United Glass Bottle Manufacturers.

THOUGH it cannot be said that the glass industry, during the year under review, has recovered from the grave depression which has prevailed in this country since 1920, there are unmistakable signs that the worst times have passed, and we may expect in the near future a revival in most branches of the trade and a concomitant increase in the activities of the glass technologist.

In the past year there has been a marked improvement in the general quality of both scientific glassware and glass containers. An interesting feature of the chemical glassware industry is the tendency on the part of some manufacturers to concentrate on the production of glasses of a higher thermal endurance and mechanical strength than were formerly manufactured in this country. This entails a sacrifice of some desirable chemical properties, notably the exceptional resistance to the action of alkalis, a property which characterised English chemical glassware from 1916 to 1921. In the opinion of those makers of chemical glassware who have modified their formulae on these lines, the average chemist will prefer to work with glassware with which he can take risks in heating and cooling, as compared to a glass which is inclined to be brittle, even though the latter glass is less soluble in his reagents.

There appears to be a growing demand on the part of users of glass containers of all descriptions for colourless or "flint" glass, and at the present time many bottle manufacturers are producing from tanks bottles equal in colour and brilliance to those formerly made from pot metal. Three years ago six samples selected from the best bottles and jars then obtainable (made in tank furnaces) showed an average iron content of 0·13% Fe_2O_3 . A similar test made recently showed an average iron content of 0·08% Fe_2O_3 .

The general improvement in quality is due partly to the growing recognition of the importance of technical control and to the absorption into the industry of technically trained men, and partly to the activities of the Glass Research Association and the Department of Glass Technology at Sheffield University.

The details of the work of the Research Association are not disclosed, but certain information is available. Investigations have been carried out at the National Physical Laboratory and at Sheffield University on behalf of the Association and also at the Association's Laboratories in Bedford Square.

The fundamental problem of the determination of the viscosity of glasses covering the whole range of temperatures encountered in glass manufacture is being undertaken at the National Physical Laboratory, while at Sheffield University among the investigations conducted have been the function of arsenic in glass, the influence of water, chlorides, and sulphates on the properties of glass, and at the Laboratories of the Research Association investigations on the electrical conductivity of glasses have been carried out. It is unfortunate in the interests of the advancement of glass technology that the work of the Research Association cannot be published, but this appears to be one of the insuperable drawbacks which must always be associated with the formation of Research Associations. A considerable portion of the work of the Association comes under the category of factory investigations, and it is to this work largely that we may look for the general improvement in the technology of the industry.

This year, as in previous years, we find that the Department of Glass Technology at Sheffield is responsible for many valuable contributions to our knowledge of glass, in spite of the fact that the time of many of the members of the staff was occupied largely by work on behalf of the Glass Research Association.

A number of papers on the manufacture and properties of some glasses containing boric oxide are given in the March and June numbers of the Journal of the Society of Glass Technology, the papers bearing the names of W. E. S. Turner, V. Dimbleby, S. English, F. W. Hodkin, and M. Parkin.¹

Three series of melts were made in 28-lb. covered pots, a melting temperature of 1400° C. being adopted. Simple glasses containing only sodium oxide, boric oxide, and silica were made, the first series containing 20% of sodium oxide, the boric oxide content varying from 0 to 45%. In the second series the sodium oxide was maintained at 10%, the boric oxide varying from 15 to 50%, and in the last series the sodium oxide content was 5%, the boric oxide varying from 20 to 45%.

In these series no evidence of the segregation of glasses into immiscible layers of differing composition, as has been suggested by earlier workers, was observed. The specific gravity and refractive index of samples were taken from different depths in the pot to corroborate this.

With a constant sodium oxide content the time required for melting decreased rapidly as the silica was replaced by boric oxide. The authors observed, however, that with these glasses the time required for melting is reduced by the substitution of sodium oxide for boric oxide if the silica is unchanged; thus a glass containing SiO_2 75%, Na_2O 10%, B_2O_3 15% required seven hours

¹ *J. Soc. Glass Tech.*, 1923, 7, 57, 73, 78; *J.*, 1923, 551A.

to melt, while a glass of the composition SiO_2 75%, Na_2O 20%, B_2O_3 5% melted in $1\frac{1}{2}$ hours. This is contrary to the general opinion held in the glass house, the opinion being that borax is more potent as a "flux" than is sodium oxide. This in fact is probably the case with certain compositions outside the range covered by these papers.

During the melting process it was found that some of the glasses showed a tendency to form a scum in the pot and in some cases stones appeared to be formed. The glasses rich in boric oxide, particularly those in the first series (containing 20% Na_2O) showed a marked tendency to a "re-boil." A copious evolution of gas was observed in some cases when the surface of the glass was disturbed by the gathering iron. This phenomenon is a common occurrence in works practice when melting glasses containing boric oxide and also with barium glasses and some others.

Considerable losses of both boric oxide and sodium oxide occurred during the melting, the percentage lost varying with the duration of the melt and the fluidity of the glasses; up to as much as 15% of the whole boric oxide content and 10% of the sodium oxide content was in some cases volatilised.

The substitution of silica by boric oxide produced a marked increase in the temperature coefficient of viscosity. The glasses high in boric oxide were too fluid to gather conveniently on the blowing iron, but set extremely quickly, forming a hard skin when marvering. In all the series when the boric oxide content reached 40-45%, gathering and tube drawing became impossible.

All the glasses in the series containing 10 and 20% Na_2O which could be drawn into tubing worked well in the blowpipe. In the series containing 5% of Na_2O , glasses containing more than 35% B_2O_3 showed evidence of devitrification, an opalescence appearing on reheating or slow cooling. A similar effect was produced in the 10% Na_2O series with more than 40% B_2O_3 .

Excessive quantities of boric oxide detracted from the durability and the following glasses were found to show signs of weathering on storage :—

| SiO_2 | Na_2O | B_2O_3 |
|----------------|-----------------------|------------------------|
| 80 | 20 | 0 |
| 40 | 20 | 40 |
| 35 | 20 | 45 |
| 50 | 10 | 40 |
| 45 | 10 | 45 |
| 60 | 5 | 35 |
| 55 | 5 | 40 |
| 50 | 5 | 45 |

The three latter glasses showed a surface film after 24 hours' storage, whereas the second and third in the list took four months to deteriorate to the same extent.

Examination of the physical properties showed that the approximately linear relations generally observed between the composition and the values obtained for physical constants did not apply to these glasses. Determinations were made of the annealing temperature, thermal expansion, specific gravity, and refractive index; the disperson was also determined. Keeping the sodium oxide constant, substitution of silica by boric oxide increases the annealing temperature, lowers the co-efficient of expansion, and increases the specific gravity and refractive index. The effect, however, is not linear, maxima or minima occurring in every case at the following concentrations of boric oxide:—

| | 20% Na ₂ O. | 10% Na ₂ O. |
|--------------------------|--------------------------------------|--------------------------------------|
| Annealing temp. (max.) | 16-17% B ₂ O ₃ | 10-12% B ₂ O ₃ |
| Thermal expansion (min.) | 16-17% B ₂ O ₃ | 20% B ₂ O ₃ |
| Sp. gr. | 16-17% B ₂ O ₃ | 10-12% B ₂ O ₃ |
| Refractive index (max.) | 30% B ₂ O ₃ | 10-12% B ₂ O ₃ |

Excepting the anomalies in the case of the thermal expansion in the 10% soda series and the refractive index in the 20% soda series, which are remarkable, there appears to be no doubt that this discontinuity in the physical properties is established. (The discontinuity in the coefficient of expansion has been observed by earlier workers.)

The following are the maximum and minimum values obtained in the series of glasses examined:—

| | 20% Na ₂ O. | | | 10% Na ₂ O. |
|---------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | Max. | Min. | Max. | Min. |
| Annealing temp. . . | 570° C. | 505° C. | 597° C. | 495° C. |
| Thermal expansion | 9.15 × 10 ⁻⁶ | 8.05 × 10 ⁻⁶ | 6.06 × 10 ⁻⁶ | 4.97 × 10 ⁻⁶ |
| Sp. gr. | 2.51 | 2.37 | 2.47 | 2.02 |
| Refractive index .. | 1.525 | 1.490 | 1.505 | 1.488 |

Interesting observations on the hardness of the glasses in these series were made. It was found that those compositions which gave the maxima or minima in the physical properties yielded glasses remarkably hard and difficult to cut with a file. It was further observed that in the 20% soda series the maximum durability to water occurred when the boric oxide content lay between 11 and 14%.

In a paper on the density of glass near its annealing temperature, S. English² has described the changes of mobility of a number of glasses over a range of about 200° in the neighbourhood of their annealing temperature. The glasses examined covered the complete range of soda lime, soda magnesia, and soda alumina glasses and in addition one soda lead silica and one potash lead silica glass. The author adopted the extension method, observing the rate of fall of a weight attached to the glass under test. He found that in all the glasses tested the temperature coefficient of

² *J. Soc. Glass. Tech.*, 1923, 7, 25; *J.*, 1923, 550A.

viscosity was approximately constant near the annealing temperature, and he obtained the equation for the mobility temperature relations $M=K.2^{1/18}$. (Twyman in 1917 suggested $M=K.2^{1/18}$.)

Although the mobility temperature curves are approximately parallel near the annealing temperature, at higher temperatures the curves diverge. In the case of the alumina glasses the curves remain more nearly parallel to the curve obtained for sodium silicate than do the soda lime glasses (the latter give a log mobility/temperature curve which is nearly linear over the range examined.) As the proportions of lime, magnesia, and alumina in the glass increase in each series the rise of temperature required to give twice the mobility increases. In the lime and magnesia series these temperatures (near the annealing point) are as follows:—

| % CaO. | Temperature interval. | % MgO. | Temperature interval. |
|--------|-----------------------|--------|-----------------------|
| 0.2 | 8° | 0 | 8° |
| 2.6 | 9° | 2.5 | 9° |
| 4.5 | 9° | 5.1 | 10° |
| 7.5 | 9° | 7.5 | 11° |
| 9.3 | 10° | 9.3 | 12° |
| 10.4 | 10° | | |
| 11.7 | 11° | | |

It will be seen that these temperature intervals are very similar in the two series. The alumina glasses and the alkali lead silica glasses give similar curves, with a temperature interval from 8° to 9°. At higher temperatures, however—about 150° past the annealing temperature—this interval increases to approximately 14°. This increase of temperature decreases as the lime, magnesia, or alumina content of the glass increases. In the lime series the temperature interval for the first five glasses shown above rises to 14°, but with the last two it remains at about 11°. In the magnesia series up to 5% MgO the temperature remains at 14°, but with 7% MgO this falls to 13°, and at 9.3% to 12°. The alumina glasses are similar in behaviour to the magnesia glasses.

In the lead glasses the interchange of sodium and potassium does not greatly affect the slope of the curves, but the soda glass was considerably the softer of the two, the annealing temperature being about 14° lower.

It appears probable that, in view of the curves obtained from these series of glasses, the workability or "sweetness" of glass depends very largely on the softness of the glass, although a large variation in the temperature coefficient of viscosity must be apparent when working the glass. In the lead glasses referred to above, the soda glass was found to be very appreciably easier to work than the potash glass, the former having an unusually long working range. In this case probably the heat lost by radiation—varying as the difference between the 4th powers of the absolute

temperatures of the glass and those of the surrounding bodies—will be the determining factor, the difference in the heat losses from the two glasses being about 25%, whereas since the temperature/viscosity curves are approximately parallel this latter factor will not exert a large influence on the relative "sweetness" of the two glasses. The author points out, however, that at higher temperatures points of inflexion in some of the temperature/mobility curves will probably occur, and then the larger deviation between the slopes of the curves will become more apparent in its effect on the workability of the glass.

Several important papers deal with the durability of glass. These papers are of importance, since there appears to be some likelihood of an effort being made in the near future to establish standard specifications for glassware, and before any satisfactory standards can be adopted a really satisfactory quantitative test for durability must be discovered.

W. L. Baillie³ considered that the autoclave furnished the most satisfactory means of estimating durability. He pointed out that the test must not be made too severe since the alkali liberated might react with the decomposition products of the glass and the estimation of the corrosion by titration of the alkalinity (the best method in his opinion) would come out too low. He advocates titration with N/500 acid using as an indicator an ethereal solution of iodocesin.

The following tests were suggested as a standard :—

| | |
|---|----------------------------|
| Resistance glass | 3 hours at 90 lb. pressure |
| Superior blown ware | 3 " " 50 " |
| Softer blown ware | 2 " .. 30 " |
| Bottles for ordinary laboratory purposes } 2 | |

He emphasised the value of increased sharpness of discrimination which could be obtained by a judicious selection of the conditions of test. This is shown in the following table, which gives the mg. of Na₂O liberated per sq. cm. in one hour from a series of six glasses of varying composition :—

| 2 Atmospheres. c (121° C.). | 4 Atmospheres. (144° C.). | 6 Atmospheres. (151° C.). |
|--------------------------------|------------------------------|------------------------------|
| 0.03 .. | 0.11 .. | 0.12 .. |
| 0.02 .. | 0.04 .. | 0.03 .. |
| 0.23 .. | 0.78 .. | 1.06 .. |
| 0.22 .. | 0.45 .. | 0.79 .. |
| 0.03 .. | 0.03 .. | 0.07 .. |
| 0.05 .. | 0.26 .. | 0.28 .. |

He pointed out that in the test at 6 atmospheres all the glasses were distinguished, whereas the tests at lower pressures, although dividing the glasses into groups, did not differentiate the glasses completely.

³ J. Soc. Glass Tech., 1923, 7, 79; J., 1923, 309A.

W. H. Withey⁴ pointed out that the autoclave might give anomalous results under certain circumstances, since the products of decomposition in some glasses seemed to protect the glass from further corrosion. The test, therefore, was in some cases really measuring not so much the rate of corrosion but the degree of protection afforded by the decomposition products under the conditions of the test. He considered that further work was necessary before the results obtained from the autoclave test could be accepted without close examination.

F. W. Hodkin and W. E. S. Turner⁵ give the results of tests carried out on a series of simple soda lime glasses. The glasses were tested at pressures varying from 2 to 25 atmospheres and losses in weight from the action of both steam and water were determined, together with the Na₂O extracted. Considering the results obtained in conjunction with the results from earlier work with glasses of widely different composition, the authors conclude that the autoclave test, while giving valuable information in certain cases, is not suitable as a single test for durability. An instance was cited where a glass which was satisfactory when tested with boiling water (compared with the best resistance glasses) broke down completely under the autoclave test. The authors emphasise the variation in the degree of attack by steam and by water under pressure, glasses containing alumina, boric oxide, and zinc oxide being little affected by steam, whereas the soda lime glasses showed more attack from steam than from water. The authors point out (and this was emphasised in the discussion which followed the paper) that the physical condition of the surface exerts a marked influence on the rate of corrosion.

Turner has pointed out that there is still much to be said in favour of testing glass in the powder form, since the results are obtained from freshly fractured surfaces and the values recorded are a more satisfactory criterion of the durability of the glass itself, apart from any influence which the physical condition of the surface may have.

An interesting observation on the variation of the physical properties of a glass surface was reported by C. N. Hinshelwood and H. Hartley,⁶ who found that when decomposing formic acid at 300° in glass vessels, using one glass, about 70% of carbon dioxide and hydrogen was obtained, while with a different glass only 16·5-19·1% was obtained.

The use of a solution of narcotine hydrochloride is advocated by H. S. Blackmore, V. Dimbleby, and W. E. S. Turner⁷ as a suitable

⁴ *J. Soc. Glass Tech.*; 1923, 7, 89; *J.*, 1923, 309A.

⁵ *Ibid.*, 1923, 6, 291; *J.*, 1923, 310A.

⁶ *Chem. Soc. Trans.*, 1923, 128, 1333; *J.*, 1923, 830A.

⁷ *J. Soc. Glass Tech.*, 1923, 7, 122; *J.*, 1923, 831A.

reagent for the rapid examination of the durability of glasses. The test is carried out as follows :—A solution of narcotine hydrochloride is heated to 100° C., and the vessel to be tested is also heated to 100° in a water bath. When the temperature of both the reagent and the vessel under test reaches 100°, 50 c.c. of the solution is introduced into the vessel and the mouth is closed with cotton wool. The vessel is kept under observation and the time taken for precipitation is noted. If a precipitate appears in less than 10 minutes the glass is unsatisfactory. If the precipitate appears after 10 minutes and increases during an hour the glass is suitable for some purposes, but not as a container of medicinal preparations. Minute needles appearing in from 15 to 20 minutes, but not increasing in quantity appreciably in an hour, denote that the glass is quite satisfactory for general use. No precipitate at all occurring during the hour indicates that the glass is of excellent quality. It is necessary that the vessel to be tested be cleaned with dilute acetic acid, distilled water, and alcohol before testing.

The question of the establishment of standard specifications for glassware has been discussed at two meetings of the Society of Glass Technology during the year. The general opinion appears to be that the time is ripe for such a step, although at present no agreement has been reached as regards the standard tests to be adopted.

It is suggested that a preliminary specification shall be framed to exclude obviously unstable glass, and it is urged that all users of glassware shall purchase on this specification. Recently a number of cases have been brought into prominence where glasses of undeniably unstable composition have been made and distributed, the resulting danger of the contents of the container being contaminated with matter dissolved from the glass being obvious.

Turner has advocated that the narcotine hydrochloride test be adopted. It has been stated, however, by other workers that the end point in that test is not sufficiently sharp to enable the test to be applied universally as a standard. It has been suggested that a test with boiling water for six hours and a subsequent titration with acid, using phenol red or bromothymol blue as an indicator, is more satisfactory.⁸

It appears that further work is necessary before a specification can be drawn up. T. Kato⁹ suggests specifications for laboratory glassware based on a large quantity of experimental work. He advocates a boiling water test of six hours, the maximum loss in weight allowable being 5 mg. per 100 sq. cm. In three hours' boiling with hydrochloric acid (12% solution) the specimen should

⁸ See L. A. Palmer, *J. Amer. Ceram. Soc.*, 1923, 6, 579; *J.*, 1923, 451A.

⁹ *J. Jap. Ceram. Assoc.*, 1923, 367.

not lose more than 5 mg. per 100 sq. cm., and in three hours' boiling with a 2% caustic soda solution should not lose more than 30 mg. per 100 sq. cm. The water obtained from the boiling water test should show no alkaline reaction with rosolic acid. Tests for thermal endurance are also given. The work merits careful consideration.

An interesting paper by A. R. Sheen and W. E. S. Turner¹⁰ discusses the influence of titania on the properties of glass. When the melting conditions are oxidising, titania imparts no appreciable colour to the glass. Under reducing conditions, however, colours ranging from a light amber to a dark brown are produced. It is desirable, therefore, that titrates be present in batches containing titania which are used for colourless glass.

The chemical properties of the titania glasses are good. In general durability they are superior to the lime glasses, resembling the magnesia glasses. The titania glasses possess lower annealing temperatures than the corresponding lime or magnesia glasses. Titania reduces the tendency to devitrification and the glasses have good working properties. The glasses exhibited a high thermal endurance. Specimens gathered from the pot did not crack when cooled quickly. Determination of the coefficient of expansion showed that the effect was not due to an abnormally low expansion. It must be concluded, therefore, that the high thermal endurance found is due to the strength or elastic properties of the glasses. Titania is used at the present time both in heat-resisting glasses and for the production of amber glasses.

The importance of cold work on the properties of glass has been noted by several workers. If subjected to deformation over a particular range of viscosity, birefringence which cannot be removed by the ordinary process of annealing is found. The present writer has observed glasses which have been worked too cold and which required heating to temperatures 150° above the normal annealing temperature to remove the birefringence seen under crossed nicols. Turner has stated that a certain glass required to be heated as much as 250° above annealing temperature to remove this apparent strain.

Startling changes in the mechanical properties of glass have been noted as a result of small alterations in the process of manufacture, by means of which the temperature gradients in the glass are controlled prior to blowing. In view of the fundamental importance of this question the recently published work of L. N. G. Filon and F. C. Harris¹¹ is of great interest. They subjected specimens of dense lead glasses to a load at a temperature of 400°; this load was held for a considerable period and the glass was then cooled

¹⁰ Soc. Glass Tech., Oct. 17, 1923.

¹¹ Proc. Roy. Soc., 1923, A103, 561; J., 1923, 774A.

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⁹ *J. Jap. Ceram. Assoc.*, 1923, 367.

Recent remarks by W. Rosenhain on the atomic structure of amorphous bodies¹³ suggest that it may be possible to account for these phenomena without the assumption of the presence of a crystalline phase. The existence of asymmetric groups of atoms, smaller than the crystal unit, may explain many if not all of the phenomena encountered in the study of the effect of the deformation of glass at its critical viscosity. However, it is premature to discuss this further at the present time.

It has been remarked that all glasses after annealing exhibit fluorescence when exposed to rays of short wave-length. With very rapid chilling, however, this fluorescence may be suppressed. J. R. Clarke¹⁴ exposed three soda lime glasses to radium emanation until the fluorescence ceased and the glasses were coloured a deep brown. The glasses were then heated at temperatures of 110°, 180°, 235°, and 350°. The fluorescence was again observed during the heating, and continued for a certain fairly definite period (which varied with the temperature and the composition of the glass) until the coloration had disappeared. Presumably this fluorescence indicates a molecular change occurring in the glass. At 110° 13 minutes elapsed before the fluorescence disappeared while at 350° it was absent in about 30 seconds. The glass containing the highest amount of lime fluoresced for 15 hours at 95°. By extrapolation it seems that the fluorescence would vanish instantaneously at the annealing temperature of the glass.

Various investigations on the permeability of vitreous bodies to gases have been made. J. B. Johnson and R. C. Burt¹⁵ find that hydrogen diffuses through fused silica in high vacua even at room temperatures. An easily perceptible rate of diffusion occurs with hydrogen at 300° and with nitrogen at 600°. There is a rapid rise in the diffusion velocity with a rise in temperature. G. A. Williams and W. B. Ferguson¹⁶ note that at 500° the rate of diffusion of helium through fused silica is 22 times that of hydrogen. Both Pyrex and Jena glass are impermeable to hydrogen, but Jena glass is permeable to helium. •

A number of papers dealing with the colour of glass have been published. K. Fuwa¹⁷ gives a series of papers relating to the colouring effect of tungsten, molybdenum, manganese, antimony, chromium, and vanadium.

Tungsten salts or oxides can be used as opacifiers in glasses, particularly in the absence of boric oxide. No coloration is produced. The presence of metallic tungsten gives a grey colour and sometimes yellow or orange tints. An excess of tungsten salts

¹³ British Association, Liverpool, 1923.

¹⁴ *Phil. Mag.*, 1923, **45**, 735; *J.*, 1923, 402A.

¹⁵ *J. Opt. Soc. Amer.*, 1922, **6**, 734.

¹⁶ *J. Amer. Chem. Soc.*, 1922, **44**, 2160; *J.*, 1922, 983A.

¹⁷ *J. Jap. Ceram. Assoc.*, 1923, 366, 370.

gives rise to glass gall on the surface of the pots. The scum consists of alkali tungstates.

Molybdenum imparts no colour to the glass. It can be used as an opacifier in glasses of suitable composition. Ammonium molybdate is the most convenient source of molybdenum to use. All molybdenum glasses have a tendency to become opalescent on reheating. With an excess of 5% a white gall of alkali molybdates is formed.

Nearly 600 meltings were carried out in the investigation on the colouring action of manganese. The effect of manganese was studied with glasses containing Na, K, Ca, Mg, Zn, Ba, Pb. Mn_2O_3 is the stable oxidised form above 530° C. in air. Soda glasses are pink, but potash glasses are not so clear with low concentrations of Mn_2O_3 . With large quantities of Mn_2O_3 the soda and potash glasses give similar results. MnO gives pale yellow or blue glasses. It is suggested that the MnO_2 dissociates into $x\text{Mn}_2\text{O}_3 + y\text{MnO} + z\text{MnO}_2$ and the conditions of melting and composition of the batch determine the values of x , y , and z and the consequent coloration produced. In general, MnO_2 produces a brown colour, Mn_2O_3 pink or purple, and MnO no colour or faint blues and greens. The addition of arsenious acid reduces the colour due to MnO_2 to a marked extent.

Antimony imparts no colour to glasses. Antimony glasses if heated in a reducing fire gives iridescent effects.

Chromium gives a yellowish-green colour. The addition of an oxidising agent increases the yellow tint, a reducing agent detracts from it. The colours produced by the addition of potassium bichromate are more yellow than if the chromium is added as chromic oxide. The composition of the glass greatly affects the colour produced.

Vanadium is similar in its effect to chromium except that the colours are more yellow. The composition of the glass makes no difference to the colour produced. The yellow colour is enhanced by the addition of oxidising agents and is retarded by reducing agents and by arsenic.

It is interesting to observe in Fuwa's work that arsenic appears to act as a reducing agent in every case.

The effect of the addition of sodium or potassium chloride on the colour of glasses is described in a patent granted to the Corning Glass Works.¹⁸ The presence of chlorides causes increased absorption at the red end of the spectrum. This effect is particularly marked in the case of glasses coloured with nickel or cobalt, more especially if boric oxide be present. It is stated that cobalt will give a pure blue or even a green if chlorides be present in suitable concentration.

¹⁸ E.P. 102,619; J., 1923, 355A.

A notable advance in the technology of the decolorising of glass is patented by W. C. Taylor (assigned to the Corning Glass Works).¹⁹ Neodymium oxide (Nd_2O_3) is used. An oxidising atmosphere is necessary for successful decolorisation and antimony or arsenic must not be present in appreciable quantities. This decoloriser is only effective in highly acid glasses, for example, those containing over 80% of silica if boric oxide be absent, or where boric oxide is present in quantities not less than about 50% of the whole constituents of the glass exclusive of silica. Any source of neodymium oxide was suitable for use, provided the other materials did not destroy the acidity of the glass. Commercial "didymium oxide" was convenient. The oxide was used in the proportion of 0·5–1% as a decoloriser; 5% yielded a pink colour (the neodymium replaced silica in the batch).

J. Mori²⁰ has investigated a series of soda lead silicate glasses and, assuming the usual formula for the coefficient of expansion $3a = \sum p_z$, and assigning the values for z obtained by Turner for SiO_2 , CaO , Al_2O_3 , and MgO (namely 0·05, 1·53, 1·53, and 0·45 respectively for the linear expansion), calculates values for PbO and Na_2O from his experimental results. He has assigned the coefficient for lead of 0·938 and for Na_2O 4·7 (Turner obtained 4·3 for Na_2O).

The following miscellaneous papers are also of importance:—“Analysis of bubbles in glass” (Ryde and Huddart, Physical Society, April, 1923); “The electrical properties of flint glass (Addenbrooke, Phil. Mag., 1923, **45**, 516); “Deformation study of silicates” (B. A. Rice, 1923, *J. Amer. Ceram. Soc.*, **6**, 525).

¹⁹ U.S.P. 1,449,793; E.P. 194,888; *J.*, 1923, 454A.

²⁰ *J. Jap. Ceram. Assoc.*, 1923, 36.

CERAMICS, REFRACTORIES, AND BUILDING MATERIALS.

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THE writer of the report for 1922 expressed the opinion that the results of the year were of a somewhat meagre character, and it is a matter of regret that the same must be said of the results for 1923. It is hardly fair to consider the ceramic industries in the same light as others, which are capable to a much greater extent of utilising scientific methods and profiting from the general advancement of chemistry, physics, and engineering. The complexity both of the materials used and of the type of work involved, prevents the direct application of many improvements of a general character made use of by other industries, and this difficulty is undoubtedly responsible for that conservative viewpoint which is usually considered typical of ceramic manufacturers.

CLAYS AND OTHER CERAMIC MINERALS.

H. H. Sortwell¹ has carried out an extremely detailed examination of some American and English ball clays. The properties considered are the water of plasticity, the volume shrinkage on drying, the residue on 120-mesh sieve, the cohesion of the plastic clay, the transverse strength in the form of bars of a dried mixture of clay with an equal weight of flint, the rate of flow as slips containing from 3 to 40% of clay, the porosity, the time required for the complete oxidation of organic matter at 750° C., the effect upon the colour when employed as a component of a standard body, the apparent and true densities, and the proportion of sealed pores, after firing to various temperatures. Six American and fifteen English ball clays were thus examined, so that the work must be regarded as comprehensive and of general utility. Apart from the sound and detailed information it gives, some of the rather anomalous results are noteworthy. Thus, in spite of the American ball clays being practically equal to the English in plasticity, they gave less strength to the body when dry, a fact, perhaps, explained by the general lower content of organic matter in American clays. The outstanding advantage of the English clays is the constancy in volume and porosity through a

¹ E.P. 192, *J. of Standards, Tech. Paper 227, 1923, 17, 153; J., 1923,*

considerable temperature range, whereas the American clays suffered variation in these respects. On the other hand, English clays affect the colour of the ware more seriously, so that for a given tone a higher admixture of American clay is permissible. This, however, entails raising the flux content to maintain a constant vitrification temperature. The body thus produced would have the advantage of being more plastic, but entails expert burning, as variations in temperature in the kiln mean differences in shrinkage.

A paper by C. E. Moore² upon the behaviour in the course of burning of Stourbridge fireclays is typical of much of the work which is being carried out at the present time. The properties of the fireclays which were brought under observation were: the volume changes, porosity, specific gravity, hygroscopicity, solubility in acids, heating curves, and dehydration. The details of this extensive examination need not be dealt with here, but the original paper should form very profitable reading for anyone directly or indirectly interested in fireclays.

Two papers have appeared dealing with the functions of colloidal plasticity in clays and related minerals,³ and the results confirm the expectation that the presence of water is essential to the assumption of the colloidal state by a part of the clay, and that this action performs a part of the work done in vitrification. Thus a plastic clay on heating undergoes a hardening without loss of the combined water, an effect which can only be ascribed to peptisation. After dehydration and above 700° C. other physical changes occur, resulting in an increased hardening of the clay. On the other hand, non-plastic clays only harden once at about 1000° C. Another effect due to the same cause is the resistance of burnt clays to disintegration forces by freezing. A clay dried at 150° C., compressed at 700 kg. per sq. cm., and then fired to 900° C. will crumble when twice submitted to a soaking *in vacuo*, followed by freezing at —15° C. The same clay containing 4% of water when compressed at the same pressure and given the same heat treatment, disintegrates on the fourth or fifth repetition of the soaking and freezing, but if it is made into a plastic mass with 21% of water and compressed only at 15 kg. per sq. cm., ten repetitions of soaking and freezing have no effect upon it. The plastic preparation, therefore, acts as the dry preparations fired to a higher temperature, the additional work done in attaining the higher temperature being expended in effecting molecular contact and equivalent therefore to the work to be done to reduce the particles of the non-plastic clay to the colloidal state.

² *Trans. Ceram. Soc.*, 1922-3, 22, 138; *J.*, 1923, 774A.

³ A. Bigot, *Comptes rend.*, 1923, 176, 91, 1470; *J.*, 1923, 184A, 658A.

F. P. Hall⁴ has studied the effect of hydrogen-ion concentration upon clay suspensions, and some very suggestive results have been obtained. With regard to the aqueous extracts of clays no relation between the p_{H} value of the extract and the nature of the clay could be observed, but the vast majority showed acidity between p_{H} 2.95 and p_{H} 6.8. A few showed alkalinity and among these was Bentonite. One generalisation, however, which could be made was that if a clay gave an acid extract on the first wash, the acidity increased with each subsequent wash, whereas if the initial reaction was alkaline repeated washings were successively lower in alkalinity. This reaction of clays is unquestionably due, at least in part, to the absorption of soluble salts, which are removed by washing with extreme slowness. The influence of hydrogen-ion concentration on the rate of settling has given numerical form to what was already largely known. The curves relating hydrogen-ion concentration with rate of settling are of an S-form, the maxima being the isolectric point or points of maximum rate of settling, while the minima are the points of maximum deflocculation. The range of ion concentration which the S curve covers, is shown by the following results for English ball clay : p_{H} water extract, 5.50 ; p_{H} at isolectric point, 2.78 ; p_{H} at maximum flocculation point, 10.96. The increase in the value of p_{H} on addition of soda to a clay suspension is less than would occur in the absence of the clay owing to adsorption, a state of equilibrium being reached in about 24 hours. That this removal of alkali from solution is due to adsorption over a certain range of concentrations is shown by the applicability to the case of Freundlich's equation, $x/m = KC^{1/n}$ where x =the solute adsorbed by m grams of solid from a solution of which the final concentration is C , while K and n are constants. Plotting $\log x/m$ against $\log C$ should, therefore, give a straight line if adsorption has occurred, and this is found to be the case in original concentrations ranging between p_{H} 7 and p_{H} 12. Above p_{H} 12, however, the rectilinear character of the relation breaks down, showing the onset of chemical action. A special interest attaches to the constant K , which represents the amount of solute adsorbed when the concentration is unity, and should be a function of the surface of the solid phase and therefore a measure of the fineness of the clay. Although the value of this constant is almost certainly affected by other factors, it is improbable that it is influenced to an extent to make it useless for the grading of clays, and consequently the list of clays arranged in order of the value of K given in the paper is of particular interest, although to English readers the small number of clays from this country included in this investigation is a matter of disappointment.

⁴ *J. Amer. Ceram. Soc.*, 1923, 6, 989 ; *J.*, 1923, 1132A.

The work of J. W. Mellor,⁵ in conjunction with W. H. Bragg and G. Shearer, is of a unique character and constitutes an attempt to lay the foundation of a new method of elucidating the reactions occurring in kaolin during firing. The established method of X-ray analysis was applied to kaolinite in various stages of burning. Dried at 100° C. this material was found to be definitely crystalline, but this crystallinity was destroyed by calcining to 700° C., such crystals as were present after this treatment being probably of colloidal dimensions. At 900° or 1000° C., however, crystallinity was again assumed, but of a different nature to both that of the kaolinite and that of sillimanite which formed at a higher temperature. This crystalline substance is at present unidentified, but the expectation is that it will prove to be alumina.

This work is admittedly tentative as far as it has gone at present, and its importance lies not in the results so far obtained, but in the fact that it forms a pioneer attempt to establish a means of investigation into the reactions of the complex silicates. For all practical purposes at the present day these reactions are unknown, and it is the opinion of many people that until a more complete answer can be given to the questions, "What are the chemical natures of the constituents of the clay?" and "What reactions do these substances undergo on heating?" the study of ceramics as a progressive science is capable only of a limited development.

R. Schwarz and D. Brenner⁶ deal with the constitution of clay from a synthetic standpoint, having studied the action of sodium silicate on aluminium chloride. It appears that, independent of excess of silica or the time of the reaction, a single compound, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$, is invariably formed, but may undergo modification after formation by adsorption of silica. Thus by increasing the dilution of the reactants the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ was progressively lowered until it approached 3 : 2, but it never actually reached this figure, the silica always being in excess owing to adsorption.

When an excess of silicic acid is present the above ratio rises, and when this excess amounts to 6 to 10 molecules of silicic acid the initial product $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot x\text{H}_2\text{O}$ invariably adsorbs silicic acid to form $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

On heating in contact with the solution the originally amorphous product assumes a crystalline character and after drying at 110° C. retains its water of constitution and generally behaves in a manner similar to, but not identical with, natural kaolin. Thus it loses the first molecule of water below 260° C. and the second between 360° and 640° C., whereas kaolin dehydrates continuously between 360° and 640° C., showing that, as regards the state of combination of one molecule of water at least, the two substances are dissimilar.

⁵ *Trans. Ceram. Soc.*, 1922-3, 22, 105; *J.*, 1923, 638A.

⁶ *Ber.*, 1923, 56, 1433; *J.*, 1923, 776A.

KILNS AND FIRING.

The number of improvements upon the design of kilns for burning ceramic ware is not large, and those that have been published do not appear to have any outstanding feature which gives ground for hope that this most unsatisfactory feature of manufacture of ceramics has approached the ideal to any appreciable extent. With regard to tunnel kilns improvements lie chiefly in the direction of the path of travel of the hot gases. Thus in one case⁷ the diameter of the kiln in the firing zone is enlarged beyond that of the preheating and cooling zones before and after it. In this portion of the kiln, side dampers and flues are provided, by the regulation of which the hot gases strike the line of trucks diagonally from each side. Alternatively a second set of dampers allows the gases, if necessary, to take up a parallel path if required.

An improvement to the same end is embodied in the patent by Woodall, Duckham, and Jones, A. M. Duckham, and A. T. Kent.⁸ A series of graduated baffles project from the roof and walls of the kilns and the trucks carry partition walls adjusted just to miss the lowest baffle. In addition to this the tables of the truck are mounted on bearings which permit the tables to move at right angles to the line, and by an ingenious combination of channel irons and bell crank levers alternately right- and left-handed the tables of the trucks are made to engage alternately with the baffles on the right and left and so forced to pass in a zig-zag course through the length of the kiln. The gas combustion chambers are situated in the side walls of the central compartments and the burnt gases leave the kiln at the inlet end, while cold air enters at the exit of the kiln and after absorbing heat from the burned ware, divides, one part being used to preheat the first two chambers and the other for the combustion of the gas.

Not a little surprising is the invention of E. Wesnick,⁹ who adopts radiant heat derived from an electrical resistor in the shape resembling a concave mirror surrounding the goods. The method sounds costly and does not conform with the generally accepted idea that the rectilineality characteristic of all radiations is not suited for the heat treatment of ceramic ware, excepting in the case of operations at the lowest temperature.

The efficiency of brick kilns has been dealt with in considerable detail by R. M. Campbell,¹⁰ and although this work may not exhibit many novel features, the results are instructive. The thermal balance sheet may be set out as follows: Total heat,

⁷ T. Seedorff, A. F. Barford, and L. E. George, E.P. 188,468; *J.*, 1923, 57A.

⁸ E.P. 190,393; *J.*, 1923, 402A.

⁹ G.P. 364,154; *J.*, 1923, 310A.

¹⁰ *J. Amer. Ceram. Soc.*, 1923, 6, 886.

expended per 1000 bricks, 27,179,788 B.Th.U. Heat to raise 1000 bricks to 212° F., 158,480 B.Th.U. Heat to raise water content of bricks to 212° F., 28,000 B.Th.U. Heat to convert water in bricks at 212° F. into steam, 196,000 B.Th.U. Heat to raise dry bricks from 212° F. to 1970° F., 1,990,056 B.Th.U. Total heat required = 2,372,586 B.Th.U. Therefore heating efficiency = 8.69%. Apart from other considerations, the problem of burning ceramic goods is shown by this figure to be one requiring urgent attention from the point of view of fuel economy.

A paper of very considerable importance from many points of view is that by B. M. O'Harra and W. J. Darby¹¹ upon the disintegration of refractory brick by carbon monoxide. Although this is, strictly speaking, a subject which should be dealt with under the heading of refractories, it is one which must also affect the ceramic industry generally. It has been long known that the reaction : C + CO₂ = 2CO is reversible and the equilibrium concentrations of this system were determined by Rhoad and Wheeler,¹² who showed that the optimum temperature range for the back reaction was between 450° and 600° C. It was also shown by Boudouard in 1899¹³ that this reaction is influenced catalytically by metallic iron. O'Harra and Darby have now proved that it is the deposition of carbon produced by the catalytic decomposition of carbon monoxide, which is the cause of the breakdown of refractory materials, the carbon being deposited around particles of iron and producing at these places an expansion of a magnitude sufficient to cause the rupture of the material. Certain refractory bricks, which gave excellent service at high temperatures, but which contained particles of ferric oxide, failed completely in an atmosphere of substantially pure carbon monoxide at temperatures between 450° and 600° C. It was shown conversely that in the absence of any reducible iron compound, no decomposition of carbon monoxide occurs and, therefore, this gas has no action on refractory bricks free from iron.

POTTERY AND PORCELAIN, BODIES, GLAZES, AND COLOURS.

The amount of headway made in this branch of ceramics, judging by the papers published during the year, is not large, although one or two results obtained have considerable interest.

I. E. Sproat¹⁴ has examined the crazing of glazes on semi-porcelain bodies with results that manufacturers of this kind of ware should find useful. In general it was not found possible to correct crazing by adjustment of the glaze or body composition without sacrificing

¹¹ *J. Amer. Ceram. Soc.*, 1923, 6, 904; *J.*, 1923, 1022A.

¹² *Chem. Soc. Trans.*, 1910, 2178.

¹³ *Comptes rend.*, 128, 98.

¹⁴ *J. Amer. Ceram. Soc.*, 1923, 6, 510; *J.*, 1923, 453A.

some of the desired properties of the ware, although the addition of "Hercules" clay to the body did so to a certain extent. The more important result is that an absorptive power of 7-12% gave a biscuit with which the tendency to craze was least, and that greater or lower porosities increased the instability of the glaze.

With regard to advancement in porcelain manufacture, mention must be made of the really great achievement of the State Porcelain Manufactory at Meissen in succeeding in the manufacture of a chime of fifty bells of hard porcelain, the tallest bell measuring about 5 ft. in height. The amount of experimentation and potting skill required to bring about this result must have been immense, and to the vast majority of ceramists any success in this adventure would have been regarded as but a dim possibility.

E. Singer and E. Rosenthal¹⁵ have made a highly detailed examination of the physical properties of hard porcelain in which the specific gravity, cubical expansion, thermal conductivity, specific heat, modulus of elasticity, hardness, crushing strength, permeability, and specific resistance were included. These are all essential characteristics of hard porcelain for one use or another, and sound ground-work, such as is provided in this paper, assists in making the invention of bodies for special purposes an inductive process.

Similarly useful is a comparison by E. Roth¹⁶ of porcelain prepared using either potash or soda spar. With regard to the former it seems a little unfortunate that a spar containing as much as 2·1% of soda should have been used, since felspar with a composition approximating to that of pure orthoclase is available. Among the interesting comparisons made are that the potash porcelains have the higher viscosity and potash spar dissolves 20% of clay against 15% dissolved by soda spar. Other useful observations are made which will be of value to anyone experimenting on hard porcelain production.

The expansion of hard paste bodies in the later stages of firing as shown by specific gravity determinations is mentioned indirectly by G. N. White¹⁷ as the cause of failure of certain types of hard porcelain. It is suggested that if this expansion occurs against the viscosity of the glaze the piece will cool in a condition of strain which may be sufficient to rend it to pieces. Strains of lower magnitude may give rise to the breaking of the piece spontaneously after some weeks, and although the appearance is in no way dissimilar to crazing it is distinguished by the crack extending right through the body.

¹⁵ *Ber. deut. Keram. Ges.*, 1920, 1, 3.

¹⁶ E. Roth, *Keram. Rundschau*, 1923, 31, 31.

¹⁷ G. N. White, *Chem. Age*, 9, 334.

Three papers from Japan—two from the Pottery Laboratory at Kioto and one from the Tokio Industrial Laboratory—contain a great deal of good work, which in spite of the fact that the materials used were derived from the Far East should be of use in western manufactories. This first report¹⁸ describes the experimental work in the preparation of several bodies with excellent potting qualities and appearance, although the Korean kaolin used contained appreciable quantities of iron. A series of magnesia potash glazes were examined and found very satisfactory, a particularly good one having the formula $(0.70 \text{ K}_2\text{O}, 0.30 \text{ MgO}) 1.2 \text{ Al}_2\text{O}_3, 12 \text{ SiO}_2$.

The second report from the same laboratory¹⁹ deals with the production of hard faience glazes, which have and impart the same appearance to faience as is possessed and produced by porcelain glazes. This was chiefly a problem of producing a good bright "hard-looking" glaze without excessive lustre, but with a certain amount of opacity.

A large number of experiments have been made, some of which involved the use of fluoride, which cannot be detailed here, but are worthy of study, especially as results in this direction should form a great asset in faience manufacture.

The third report²⁰ consists of a detailed examination of Japanese and European porcelains chiefly from the microstructural standpoint. The paper is profusely illustrated by photomicrographs which enable interesting comparisons to be made between the felspathic bodies, both European and Japanese, and that type of Japanese body prepared with weathered liparite or quartz-porphyry. As a general rule the sillimanite formation is higher in the European bodies, and as a corollary the Japanese are higher in translucency.

A detailed study of antimony lead glazes which will help to standardise the manufacture of yellow glazes to a considerable extent has been carried out by W. Rohn.²¹ That magnesia in some obscure way is not equivalent to the alkaline-earth oxides is once more demonstrated in this work, since whereas lime, strontia, and baryta destroy the yellow colour very effectually, magnesia only changes the shade. The best results are obtained with only soda and lead oxide as the basic constituents, as for instance in the formula $(0.80 \text{ PbO}, 0.20 \text{ Na}_2\text{O}) 0.15 \text{ Al}_2\text{O}_3, (2 \text{ SiO}_2, 0.4 \text{ B}_2\text{O}_3)$ and 3% of antimony dioxide, which gave excellent results.

Further work has been done on the replacement of stannic oxide as an opacifier,²² and the conclusions arrived at are based upon a very reliable method of measurement of opacity. Although

¹⁸ M. Akatsuka, *Rep. of the Pottery Lab. Kioto*, 1923, **1**, 1.

¹⁹ *Ibid.*, 1923, **1**, 14.

²⁰ *Tokio Industrial Lab. Rep.*, 1922, **27**, (6), 59.

²¹ *Keram. Rundschau*, 1923, **31**, 31.

²² R. R. Danielson and M. K. Frehafer, *J. Amer. Ceram. Soc.*, 1923, **6**, 634 · *J.*, 1923, 605A.

stannic oxide still remains the best material, zirconium oxide and sodium antimonate approach it very closely. The fourth in order is zirconium silicate, although impurities affect the efficacy of this substance very considerably. Some very instructive curves are given showing the power of reflection relative to magnesium carbonate for light of various wave-lengths.

In this connexion a new method of preparation of pure zirconia is of interest,²³ and also a paper on the production of white glazes using zircon by P. P. Budnikow.²⁴

Although admittedly possessing little prospect of commercial success,²⁵ the invention of a turquoise glaze insoluble on the finished piece, which in consequence becomes impervious to water, has scientific and artistic merits. After repeated failure the following glaze composition was devised : ($\text{Na}_2\text{O}=0.6$, $\text{K}_2\text{O}=0.1$, $\text{CaO}=0.3$), $\text{SiO}_2=2.8$, to which 15-27 parts of copper oxide was added. Of the bodies which carried this glaze satisfactorily, one composed of Cornish stone (17%), Tennessee ball clay (15%), cryolite (8%), and flint (60%) is typical. In the glaze the oxides Na_2O and K_2O are interchangeable without affecting the colour, but any addition of Al_2O_3 , PbO , BaO , or MgO gave greenish shades. The burning, both of body and glaze, was carried out at cones 09-06.

The use of ammonium uranate²⁶ for the production of red and scarlet glazes has been extended with success. A whole series of colours, ranging from vermillion to orange and reddish-brown, have been obtained by proper adjustment of the firing conditions and the composition.

The literature upon the subject of high-temperature glazes has been extended further by a paper by R. Twells²⁷ who has investigated three series of these glazes. Starting with the original formula (0.3 K_2O , 0.7 CaO), 1.3 Al_2O_3 , 11.0 SiO_2 , the first series is derived by the equivalent of lime being replaced triaxially by magnesia and baryta. The result of the substitution is practically negative if small variations in the vesicularity of the glaze be overlooked. In the second series the same original formula is varied by the mutual triaxial replacement of the three clays employed, namely, Florida and North Carolina kaolins and Kentucky ball clay. It was found that the only notable result of this variation was the lowering of the maturing temperature by the ball clay. For the third series a new formula was used, namely, 0.2 K_2O , 0.8 CaO , 0.8-1.6 Al_2O_3 , 8.0-14.0 SiO_2 for which the usual diagrams have been mapped out. There is much information in this paper

²³ H. von Siemens and H. Zander, *Wiss. Veröffentl. Siemens-Konzern*, 1922, 2, 484; J., 1923, 143A.

²⁴ P. P. Budnikow, *Tonind. Ztg.*, 1923, 47, 173.

²⁵ M. M. French, *J. Amer. Ceram. Soc.*, 1923, 6, 405; J., 1923, 270A.

²⁶ M. Akatsuka, *Rcp. of Pottery Lab. Kioto*, 1922, 1, 57.

²⁷ *J. Amer. Ceram. Soc.*, 1923, 6, 1113; *Abstr.*, 1924, B, 57.

which will be of the greatest use to manufacturers of these high-fire products, but in the opinion of the writer, a mistake has been made in not working with reasonably pure materials and, having once established the principles and main facts with these, replacing them according to analysis with more commercial products, either altogether or step by step. As the work now stands, the formulæ given above are fictitious and differ considerably from what would be obtained from analysis. Any one wishing to repeat one of these glazes would either have to find a spar of the same composition as that used in this work and to add it in such quantities as would be required if it were pure orthoclase, or, what would be far more rational, to take the analyses given by Tewells and re-calculate his formulæ, so making the results independent, or as nearly so as possible, of the nature of the spar.

REFRACTORIES.

A very large amount of work continues to be done on the subject of refractories, both as regard the method of manufacture and the nature of their composition. The number of new refractories which continue to be patented is large, and of the majority the distinctive qualities appear to be somewhat obscure, although a serious judgment cannot be made without direct experimentation. The most hopeful feature of the year's work is that afforded by investigations into the physical chemistry of certain well-known refractories, and based upon these results some real progress in this field may be looked for.

On the practical side it is significant to note that electrically-sintered magnesite is being produced in quantity by the Carborundum Co., of Niagara Falls. Carefully selected magnesite, containing 95% of magnesia and less than 1% of iron oxide, is fused in an electric furnace, with the result that it undergoes no contraction when put to industrial use. Its melting point is given as 2600° C. Another form of magnesia refractory, patented by the General Electric Co.,^{27A} is stated neither to expand nor to contract to any appreciable extent up to 1800° C.; it consists essentially of crystalline calcined and sublimed magnesia specially compounded.

W. J. Rees very aptly comments on the situation of the subject of refractories at the present time.²⁸ He insists that the only sound basis on which to compare refractories is the cost of refractories per ton of output of saleable product. There is much to be said for this view, particularly that it would emphasise the applicability of the refractory and reduce the present tendency of claiming that this or that composition is the best for any purpose. The paper in question contains a good deal of useful matter, although

^{27A} U.S.P. 1,444,527; J., 1923, 310A.

²⁸ *Colliery Guardian*, 125, 515.

the subject is considered more from the user's than the producer's standpoint.

The same author has published²⁹ a comparative examination of different refractories as regards their utility in coke-oven practice. The materials were exposed to the action of salt vapours at 800°–1200° C., and the results show that the degree of corrosion was chiefly connected with the porosity, which allows the penetration of sodium chloride and other inorganic vapours into the interior of the bricks. The result of this penetration is to form a vesicular structure, which opens up the inner surfaces to further attack. Highly silicious materials are, therefore, more suitable for coke-oven practice.

The preparation of carbonised bricks by new methods has given some very promising results.³⁰ Raw clay is placed in a muffle furnace in presence of coal, so that at the same time that the clay attains its maximum porosity the atmosphere surrounding it is heavily charged with carbonaceous vapours, which penetrate it and deposit carbon in its pores. On further rise in temperature the clay shrinks and compresses the enclosed carbon to an extent to give it a density comparable with that of steel. On heating in an oxidising temperature the black carboniferous brick loses its carbon content, burning white, while its thermal properties undergo a radical change, the black brick having a high and the white a low thermal conductivity. The high conductivity for heat and its great hardness make this carbonised clay a highly attractive proposition, and it is hoped that further work upon it will be forthcoming.

The resistance of magnesite, chrome, silica, diaspore, and fire-clay to the action of five different slags formed the basis of the work of R. M. Howe, S. M. Phelps, and R. F. Ferguson.³¹ Their method of grinding both the refractory and the slag and mixing the two in varying proportions for testing the fusion point in the form of cones has given some interesting results, although it is not incapable of adverse criticism. Obviously the conditions obtaining in ground mixtures of the two components are far removed from those under which corrosion usually occurs, and rather than the melting point of the product of the action of slag upon the refractory being the most potent factor, it might be argued that the solubility of the refractory in the slag was the more important property. However, a number of interesting results are given which quite possibly will be found of value.

A very appreciable contribution to knowledge of the behaviour of refractories on heat treatment is afforded by the work of H. S. Houldsworth and J. W. Cobb,³² who have examined the

²⁹ W. J. Rees, *Fuel*, 1922, 1, 20.

³⁰ W. Smith, *Brit. Clayworker*, 1923, 32, 17.

³¹ *J. Amer. Ceram. Soc.*, 1923, 6, 589; *J.*, 1923, 45A.

³² *Ibid.*, 1923, 6, 645; cf. *J.*, 1922, 709A.

reversible thermal expansion from 15° to 1000° C. of kaolin, silicious and aluminous fireclay, quartzite, alumina, magnesia, and carborundum. The materials were first subjected to a preliminary burning at temperatures ranging from cone 06 to cone 20, and were then heated in a resistance furnace to 1000° C., the expansions or contractions over this period being measured very accurately, and plotted against the temperature. By this means the authors are able to form some valuable conclusions as to the silica conversions in the firing process.

The conversion of α - into β -quartz is responsible for the very large expansion which Welsh quartzite shows from 550° to 600° C. Firing to cone 9 converts a part of the quartz into cristobalite, and for this reason the expansion occurring between 200° and 250° C. is increased. The expansion of this range is still further increased by two hours' firing at 1400° C. with concomitant decrease in the expansion at 550° C. The overall result is that by suitable heat treatment Welsh quartzite can be obtained in a form in which nearly the whole of the expansion occurs between 15° and 300° C., thereafter the increase in volume being a small fraction of the whole. Therefore a furnace made of bricks in which the cristobalite conversion was complete would require judicious treatment up to a temperature of 300° C., but having passed that point any fluctuation between 300° and 1000° C. is without effect. On the other hand, if quartz is present any fluctuation between 15° and 600° C. is accompanied by considerable volume changes. To convert the whole of the quartz into cristobalite a two hours' heating at 1530° C. was necessary in addition to the previous heat treatment, although to effect the same change with flint two hours' heating at 1380°-1400° C. was sufficient.

The examination of a silica brick after use in a steel furnace showed the presence of α - and β -quartz towards the end of the brick away from the interior of the furnace, while the opposite end was composed almost entirely of cristobalite, showing that the conversion had occurred in use. Similar tests on a brick from a coke-oven show that the coefficient of expansion of the outer layer was double that of the inner layer, a point graphically represented in the paper and effectively demonstrating the cause of internal stresses when a furnace of such bricks is heated.

It is not without interest to compare this work with a research along similar lines by Y. Tadokoro,³³ who, however, has carried his investigations to higher temperatures, namely, 1300° C. instead of 1000°. The results are substantially in agreement with those of Houldsworth and Cobb, and the two papers together form a useful combination.

³³ *J. Amer. Ceram. Soc. Abstracts*, 1923, 8, 159.

Reference may be made here to the work reported under the heading of "Kilns and Firing," by O'Harran and Darby³³ dealing with the disintegration of refractories by deposition of carbon from its monoxide, and it must be emphasised that in all improvements in this field, proper consideration must be given to this fact, so largely overlooked hitherto, which means that a refractory, no matter how excellent in properties, will fail in the presence of carbon monoxide below 600° C., if contaminated with particles of iron, in the metallic or reducible form.

Among the noteworthy contributions to the work of the year must be placed the "Progress Report on Specifications for Refractories,"³⁴ which constitutes an attempt to determine specifications for use by the various United States Government departments when purchasing refractories. The tests applied were devised in such a way as to fall into two groups—(a) suitability test and (b) control tests. The former group consisted of an endurance test, a constant-volume test, and a quenching test, while a fusion point test and a load test formed the basis of control. It is unnecessary in this report to go into details of these methods, for these and the comparative results obtained by the treatment of 41 samples of the refractory brick are discussed and criticised in the original report at some length. The value of the publication to users of refractories in England lies chiefly in the very excellent idea which is given of the type of result which should be obtained from a good-quality refractory for any particular purpose and in the fact that it might be taken as the basis of a similar system of testing in this country.

BUILDING MATERIALS.

The year under review has witnessed the institution of the Stone Preservation Committee of the Building Research Board to report on the best methods by which decay in building stones, especially in ancient structures, may be prevented or arrested. The question of the deterioration of stonework in buildings is a matter of general economic importance. But in the cases of our historic buildings and ancient monuments prevention of the serious decay and gradual demolition of tooled surfaces and main structures constitutes a special problem which has engaged the attention of many investigators for a considerable time, without, however, finding any generally satisfactory solution. The constitution of this committee is such as to permit the expectation that any conclusions arrived at in due course will be of great practical utility.

With regard to the progress during the year in the manufacture of building materials, the chief innovations relate to that of cement, and among the important literature which has been published is

³³ *J. Amer. Ceram. Soc.*, 1923, 6, 1098.

Pamphlet 1 of the British Portland Cement Research Association. The subject dealt with in this pamphlet is the variation of the time of setting with chemical factors, and it is proved beyond all doubt that the setting time of cement undergoes no change *per se*, as when stored out of contact with air or water. It was also unaffected by dry air, oxygen, or ozone, but accelerated considerably by dry carbon dioxide.

In the moist state carbon dioxide produces a very great decrease in the setting time (and also alters the character of the cement), while moist air prolongs the setting time. The time of set has been found to depend upon the proportion of combined water present in the hydrated calcium aluminate or silicate, which is considered to form a protective layer around the particles, retarding the penetration of water into the interior. The higher the proportion of combined water in the cement, the more impervious is this surface layer, and therefore the presence of water, as in the case of moist air, occasions retardation of setting. Conversely, the removal of water, whereby the surface layer is disturbed or weakened, results in the time of set being reduced, as is shown by the effects of sodium, potassium, and even ammonium carbonates, certain sulphates, and borax. Chlorides had little effect and nitrates none at all. Although in certain cases the action of soluble salts on cement is definitely a chemical one, double salts, for instance, being probably formed when calcium sulphate is added, it cannot be said that this is always so, and it may be ultimately proved that the action is in general catalytic.

A notable result is that in some instances the presence or absence of water of crystallisation in the added salt was the determining factor in the time of setting. The main object of the research was to determine the action of gypsum as a retarder of setting, and the conclusion arrived at is that its action is irregular and uncertain. In this respect retardation by steam or water is considered preferable.

The thermal reactions occurring during the drying and burning of cement have been examined by R. Nacken,³⁵ who finds that the heat of reaction undergoes a slow increase after the carbon dioxide has been expelled until at a temperature of 950° C., the maximum value of 600 calories per gram is attained. It appears that the slow reaction is the expulsion of carbon dioxide, and that when this is complete the formation of calcium silicates and aluminate is relatively rapid and occurs at the greatest rate at about 960° C., the condition of equilibrium being reached very quickly.

Another contribution to the study of the setting of cement is given by S. N. Brown,³⁶ who considers the subject from first principles and goes on to make some interesting remarks. The chief

³⁵ Zement, 1922, 11, 245, 257; J., 1922, 815A.

³⁶ Chem. Trade J., 1923, 72, 127.

agent in the setting of cement is considered to be alumina, an increase in the content of which is accompanied by an augmented speed of set, and it is because gypsum removes alumina from solution that this substance functions as a retarder. The helpful observation is made that the contamination of the cement by the ash from the fuel used in burning will affect the setting time adversely through its content of salts, and it is because of the absence of ash in rotary-kiln cements that 1-2% of gypsum is usually added to produce a product with a normal setting time. It is maintained that 50% of Portland cement consists of material in so large a state of division as to be replaceable by sand.

E. Berl and W. Urban,³⁷ working with pure precipitated materials, have studied the crushing strengths of cements made up of lime, alumina, and silica after being allowed to harden without heat treatment. The maximum crushing strengths of mixtures of each pair of constituents in varying molecular proportions were measured first and then complex mixtures containing the three components were studied. The paper might be easily considered as too academic for practical application, but although this is true to a certain extent, the results obtained have a bearing of definite value upon cement research.

Much work continues to be done on the question of the waterproofing of cement, and it is highly satisfactory to note that the College of Technology of Manchester has obtained such good results from the substitution of some of the sand in cement with the preparation called Kynazite.³⁸ Not only was the waterproofing sufficiently good to withstand water under pressure, but the compression tests on the product showed an increase in strength. If, however, the whole of the sand was replaced by Kynazite the strength was reduced to 50% of that of plain concrete, but the imperviousness was of a very high order.

Some useful results establishing the relation between the temperature of drying plaster and its absorptive power have been obtained by P. Jolibois and P. Lefebvre,³⁹ the absorptive power being measured by the capability of the plaster to absorb iodine vapour. This property was progressively lowered by drying at increased temperatures, until it was reduced to a negligible quantity by desiccation at 800° C. These experiments and others upon the absorption of water by plaster dried between 120° and 300° C., were carried out with an accuracy which gives a high degree of reliability to the results obtained.

³⁷ *Z. angew. Chem.*, 1923, **36**, 273; *J.*, 1923, 777A.

³⁸ Anon., *Chem. Age*, 1923, **8**, 238.

³⁹ *Comptes rend.*, 1923, **176**, 1476; *J.*, 1923, 659A.

IRON AND STEEL.

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The question of production in the iron and steel industries is of such vital importance, that the tables given in the last two reports are continued here, the figures being taken from the Bulletins of the National Federation of Iron and Steel Manufacturers :—

Production of Pig Iron in the United Kingdom.
 (In thousands of tons.)

| Month and year. | Hæmatite. | Basic. | Foundry. | Forge. | Total including alloys and other qualities. |
|--------------------|-----------|--------|----------|--------|---|
| 1922 : | | | | | |
| Oct. | 129.9 | .. | 151.1 | .. | 134.0 |
| Nov. | 148.6 | .. | 145.0 | .. | 134.9 |
| Dec. | 179.0 | .. | 153.2 | .. | 136.1 |
| 1923— | | | | | |
| Jan. | 186.1 | .. | 180.0 | .. | 138.6 |
| Feb. | 174.0 | .. | 184.8 | .. | 125.9 |
| March | 206.3 | .. | 204.6 | .. | 144.7 |
| April | 226.4 | .. | 207.2 | .. | 144.7 |
| May | 252.1 | .. | 217.9 | .. | 158.8 |
| June | 246.7 | .. | 215.2 | .. | 146.5 |
| July | 218.9 | .. | 200.6 | .. | 147.2 |
| Aug. | 184.4 | .. | 186.6 | .. | 154.7 |
| Sept. | 165.2 | .. | 182.6 | .. | 151.1 |
| | | | | | 24.0 |
| | | | | | 558.6 |

Production of Steel in the United Kingdom.
 (In thousands of tons.)

| Month and year. | Open-hearth. | Bessemer. | All other ingots and castings. | Total. |
|--------------------|--------------|-----------|--------------------------------------|--------|
| | Acid. | Basic. | Acid. | Basic. |
| 1922— | | | | |
| Oct. | 167.0 | 360.0 | .. | 15.6 |
| Nov. | 175.9 | 384.3 | .. | 18.8 |
| Dec. | 163.1 | 348.1 | .. | 17.6 |
| 1923— | | | | |
| Jan. | 183.2 | 398.6 | .. | 31.1 |
| Feb. | 235.4 | 428.7 | .. | 24.7 |
| March | 262.7 | 493.2 | .. | 23.0 |
| April | 225.0 | 473.9 | .. | 25.8 |
| May | 273.0 | 485.2 | .. | 38.5 |
| June | 226.5 | 475.4 | .. | 44.1 |
| July | 185.1 | 402.1 | .. | 33.2 |
| Aug. | 164.0 | 357.2 | .. | 31.0 |
| Sept. | 194.0 | 444.7 | .. | 37.8 |
| | | | | 9.3 |
| | | | | 9.3 |
| | | | | 695.1 |

It will be seen from these tables that the improvement indicated in the last report continued more or less steadily until June and that the figures show considerable increases over those published

last year. The steel production figures are particularly interesting, as they indicate the increasing relative importance of the basic open-hearth process over the acid process, and the decreasing value of the basic Bessemer process as a steel producer.

MANUFACTURE OF IRON.

In connexion with blast-furnace practice, chief attention seems to have been given during the past year to such questions as the preparation of the charge for the furnace, the cleaning of the blast-furnace gas, the treatment of flue dust and fuel economy. There is little to report as regards new plant, but this was to be expected from the continued depression in trade. The new furnace recently installed at the Clarence Iron Works, Middlesbrough,¹ is 85 feet high, is equipped with a battery of seven dust catchers, a Wrightson Ringquist type charger for buckets holding 8 tons of ore or 3 tons of coke, 6 Cowper stoves, and a Kling-Weidlein type gas cleaner, comprising four units, each of a capacity of 15,000 cubic feet per minute. There is also a sintering plant with an output capacity of 600 tons of sintered ore in 24 hours, and a plant for the manufacture of slag bricks. This plant is thus a typical example of the modern tendency to improve methods of charging, gas cleaning, efficient heating of blast, preparation of fines, and utilisation of slag.

Chemical methods of iron ore purification are described by A. J. Moxham,² who has carried out an investigation extended over many years. In the preparation of the charge for blast furnaces by sintering, R. L. Lloyd³ states that sinter of very poor quality is obtained from flue dust containing too much carbon, in a Dwight-Lloyd furnace. The plant works at its maximum capacity and the product is strongest when the fines contain 8% of coke, and dust containing larger percentages should be mixed with pyrites cinders or fine ores to reduce the carbon to this figure. The product in all cases is a coke-like mass of ferroferric oxide, which is extremely porous and eminently suitable for blast-furnace work, being quickly reduced by the gases; in addition, practically all the sulphur is removed during the sintering process. Another process used for the briquetting of flue dust, the so-called corrosion process, is described by A. L. Stillman.⁴ The term "corrosion" is used because an acid agent, such as wire-mill liquor or a solution of copperas, is employed to act on the ferrous oxide present in the flue dust, resulting in the formation of iron sesquioxide, which acts as a dense, hard, waterproof binder.

¹ *Iron and Coal Trades Rev.*, 1923, 106, 111.

² *Iron Age*, 1923, 111, 31.

³ *Min. and Met.*, Oct., 1922; *J.*, 1922, 899A.

⁴ *Iron Age*, 1922, 110, 1571.

The changes which take place in the composition of blast-furnace gas during the blowing-in and blowing-out of furnaces and also during the change of charge mixtures have been studied by P. Greimer.⁵

Easily reducible ore charges increase the CO₂/CO ratio, whilst refractory ores diminish it. The change in the CO₂/CO ratio on charging a new mixture is completed in two steps, one in a zone at about two-thirds the height of the furnace and the second at about the position of the boshes or hearth. From the position of the two changes in composition of the gas, the blast furnace may be divided into three reduction zones, in which the following reactions occur respectively: indirect reduction by means of carbon monoxide, mixed indirect and direct reduction, and direct reduction by means of carbon.

The cleaning of blast-furnace gas is dealt with by F. E. Kling,⁶ especially as regards dry-hot cleaning. This method of cleaning has many advantages over wet-cold cleaning in that the sensible heat of the gas is retained, no water is required and therefore no settling tanks. The labour costs in handling the dust are less and the dust can be sintered and briquetted immediately, while sludge from the wet process has to be dried. Full details are given for a Halberg-Beth plant and a Kling-Weidlein plant with a capacity of 3,500,000 cub. ft. per hour. The first cost and operating cost of the latter plant are much lower but the degree to which the gas is cleaned is much higher in the Halberg-Beth plant, being 0.004 grain as compared with 0.3 grain of dust per cub. ft. in a single-stage Klein-Weidlein and 0.1 grain in a two-stage cleaner.

The desulphurising power of iron blast-furnace slags has been studied by R. S. McCaffery and J. F. Oesterle,⁷ who determined the solubilities of calcium and manganese sulphides in calcium bisilicate, anorthite, and gehlenite in the temperature range 1350°–1600° C. The curves obtained show a marked increase in the solubilities with rise of temperature. In the blast furnace, desulphurisation of the metal is promoted in the hearth by contact between metal and slag and the presence of large quantities of low-sulphur slag on the metal should be beneficial, hence the number of slag runnings between the casts should be reduced to a minimum.

The reactivity of coke as a factor in the fuel economy of the blast furnace has been studied by E. R. Sutcliffe and E. C. Evans.⁸ The highest carbon duty in a blast furnace is given by a fuel which possesses the greatest capacity for combustion in extremely dilute oxygen, as exemplified by the superiority of charcoal over metal-

⁵ *Stahl u Eisen*, 1923, 43, 681; *J.*, 1923, 779A.

⁶ *Blast Furnace and Steel Plant*, 1923, 11, 44.

⁷ Amer. Inst. Min. and Met. Eng., Aug., 1923; *J.*, 1923, 932A.

⁸ *J. Iron and Steel Inst.*, 1923, 107, 27; *J.*, 1923, 552A.

lurgical coke. An "active" coke having minute cells with thin cell walls can be produced by the slow carbonisation of briquettes made from a finely divided coal mixture. Using a suitable method of production, a fuel can be obtained possessing a hardness equal to that of metallurgical coke, a density approaching that of coal, and a reactivity of the order of that of charcoal.⁹ The use of such a fuel would concentrate the process of reduction nearer to the hearth, less limestone would be required and less volume of blast would be necessary with consequent reduction in the sensible heat leaving the furnace. Owing to the increased amount of direct reduction, the carbon requirements of the furnace would probably be much lower than is normally the case and the output of the furnace would be increased.

The combustion of coke in the blast furnace hearth is also dealt with by G. Perrott and S. P. Kinney,¹⁰ who give the results of a number of experiments made at eleven blast furnaces in which the composition of the gases was determined by means of water-cooled gas-sampling tubes driven through the tuyères.

The forms of sulphur in coke and their relations to blast-furnace reactions are discussed by A. R. Powell.¹¹ There are four characteristic sulphur constituents of coke, viz., ferrous sulphide, absorbed free sulphur, sulphates, and sulphur held in solid solution in the carbon. In the reduction zone of the furnace the free sulphur forms ferrous sulphide and the sulphates are reduced and also form ferrous sulphide. In the zone of spongy iron, a considerable amount of sulphur is taken up by the iron from the coke. The removal of ferrous sulphide from the coke or its conversion into calcium sulphide by liming the coke, largely eliminates this absorption of sulphur. In the zone of preliminary slag formation and in the combustion zone, the absorption of sulphur by the iron is largely prevented and the iron is desulphurised by the slag. In the combustion zone the slag also removes from the iron, the excess sulphur which entered the iron in the spongy iron zone.

The fast driving of Cowper stoves by the Pfoser-Strack-Strumm process, with a view of cutting down the number of stoves necessary and increasing the efficiency of the process of heating the blast, is described by P. Lemoine.¹² The process consists of increasing the rate of the passage of the products of combustion in a modified Cowper stove, in order to obtain, without any increase in the temperature of the waste gases, either a diminution in the period of heating, or, given equal periods of heating, an increase in the blast temperature, or both results simultaneously. Special

⁹ Cf. J., 1922, 196t, 492A.

¹⁰ Amer. Inst. Min. and Met. Eng., Feb., 1923.

¹¹ Ibid., Feb., 1923; J., 1923, 455A.

¹² Rev. Mét., 1923, 20, 88; J. Iron and Steel Inst., 1923, 107, 642

arrangements of the refractory bricks are required and an accessory installation of blowing appliances and fans. Tests have shown advantages for octagonal bricks over hexagonal bricks in the stoves.

MANUFACTURE OF STEEL.

There are no outstanding developments to be reported in connexion with the methods used for the production of steel, but much useful information is being accumulated as a result of detailed organised investigation of steel-making processes. This is particularly the case with regard to the open-hearth process which is by far the most important of the processes, and such questions as reactions in the furnace, composition and functions of the slags, manurial value of basic slags, etc., have received a considerable amount of attention.

According to C. C. de Coussergnes,¹³ the most important factor in steel manufacture is the attainment of the highest possible temperature and, therefore, it is necessary to heat up the bath rapidly to the highest required temperature. He points out, however, that the selective action of oxygen leads to different reactions at different temperatures and these require careful investigation before the best practice can be obtained. In the quick driving of basic open-hearth furnaces three periods should be recognised, viz., period of formation of slag and oxidation, period of deoxidation by phosphorus, and period of deoxidation by carbon. A study has been made of the basic open-hearth process, especially with regard to the oxygen content of the steel produced and its influence on the properties, by H. Monden.¹⁴ The oxygen content is derived chiefly from the charge and is highest when the greatest quantity of old rusted scrap is used.

The behaviour of manganese in basic open-hearth furnaces has been investigated by P. Oberhoffer and F. Kœrber,¹⁵ especially with regard to the conditions under which it is re-absorbed from the slag by the steel. There appear to be no simple relations between the manganese reduction and the following factors, such as have been previously suggested : the basicity of the slag, the addition of oxides, the form in which manganese is added, the ratio between manganese oxide and iron oxide in the slag and metal, and the actual amount of oxide of iron in the slag. No relation was found between the amount of carbon in the steel and the oxygen combined with the manganese and iron, but it is suggested that the amount of oxygen in the air introduced for combustion has some effect.

¹³ *Rev. Mét.*, 1922, **19**, 639 ; *J. Iron and Steel Inst.*, 1923, **107**, 666.

¹⁴ *Stahl u. Eisen*, 1923, **43**, 745 ; *J.*, 1923, 778A.

¹⁵ *Ibid.*, 1923, **43**, 329 ; *J.*, 1923, 456A.

The constitution of basic open-hearth slags and its relation to furnace reactions has been studied by T. P. Colclough.¹⁶ The rational analysis of a number of melting slags of varying composition showed that the fundamental slag in a basic open-hearth furnace is composed of calcium tetraphosphate with a monosilicate, in which lime, magnesia, or manganese may be the basic radicle. The type of compound is not altered by adding basic oxides, which merely pass into solution, but lime may replace manganese oxide, which in turn may be reduced to manganese under certain conditions. The amount of excess of base present is very important, as the amount of phosphorus oxidised depends entirely on the excess of base present above that required to form a monosilicate with the silica present, and further addition of lime will therefore cause a preferential removal of phosphorus, rather than of carbon. The removal of sulphur from the molten metal is not directly due to the presence of free lime in the slag, but to the action of manganese which has been replaced from the slag by lime.

It is known that basic open-hearth fluorspar slags, as far as their fertilising properties are concerned, cannot be compared with the older Bessemer slags and that the citric-solubility test is entirely empirical; the investigation carried out by D. N. McArthur¹⁷ on the constitution and manurial value of low-grade basic slag should, therefore, be of value. The slag experimented with was obtained from an ordinary charge made from basic pig iron and steel scrap, fluorspar being used. The conclusions arrived at are: (1) Open-hearth fluorspar slags of low phosphorus content have a distinct fertilising value in their lime content and could be used to replace ground limestone in agricultural practice. (2) The fineness of division of a slag is important, the finely ground material being more beneficial than the coarsely ground material.

In connexion with the Bessemer process, E. Spetzler¹⁸ has pointed out that the physical properties of basic Bessemer steel depend more on the temperature at which it is blown, than on the chemical composition. He gives the results of an investigation into the sources of the loss of heat of the iron from the blast furnaces through the mixer to the converter and some details of the means employed to reduce this loss.

An interesting inversion of the ordinary Bessemer process is suggested in a patent by A. P. Heyn.¹⁹ Waste slag, for example, the product from the smelting of non-ferrous ores containing an appreciable quantity of iron, is smelted with a suitable mixture of rich iron slags or ore, in order to give a silicate slag of low melting

¹⁶ *J. Iron and Steel Inst.*, 1923, **107**, 267; *J.*, 1923, 553A.

¹⁷ *J.*, 1923, 213T.

¹⁸ *Stahl u. Eisen*, 1923, **43**, 1315; *J.*, 1923, 1179A.

¹⁹ E.P. 193,475; *J.*, 1923, 407A.

point, the iron in which is reduced to the metallic state by the passage of reducing gases through the molten mass.

A comparison of American and English methods of producing high-grade crucible steel is made by T. H. Nelson,²⁰ who states that 80% of the crucible tool steel made in Sheffield is still produced in coke-hole furnaces using clay pots. In America, gas-fired furnaces and plumbago pots are always used. The plumbago pots give 5 to 10 heats as compared with 3 from clay pots. The disadvantage of the plumbago pots lies in the fact that carbon is absorbed by the liquid steel and it is not possible to forecast with any degree of accuracy to what extent this carbon absorption will take place. By the introduction of ladle teeming a greater degree of uniformity has been established. The comparative production figures are English practice, 4500 lb. in three heats; American practice 18,000 lb. in six heats.

FOUNDRY PRACTICE, CASTINGS, ETC.

In general foundry practice, although there is nothing of outstanding importance to be reported upon, a considerable amount of attention has been given to questions relating to moulding sands, arrangement of moulds, temperature of pouring, etc., with a view of improving the quality of castings, cutting down the number of wasters, and thus leading to increased efficiency of the processes involved. Volume changes of castings on solidification, influence of impurities on shrinkage and segregation, internal chill in castings, etc., have also received attention.

Some of the characteristics of moulding sands have been dealt with by J. E. Fletcher,²¹ who has described a method of indicating these characteristics by subsidence curves.

The contraction of iron during solidification is a matter of very great importance and an exact knowledge of the various factors which influence the amount of contraction is most desirable. The influence of various elements in this direction has been studied by F. Wüst,²² who shows that the contraction of pure iron from the solidifying temperature is 2.39%. It is diminished by carbon, 1.7-2% of this element giving minimum contraction of 1.9%, but this increases as the carbon is further increased. Phosphorus diminishes the contraction to 1.3% at 1.7% P and further additions increase it. Silicon diminishes the contraction to 1.7% at a content of 18.24% Si. Manganese was the only element found to increase the contraction, which rose to 2.89 at 15.5% Mn. Sulphur diminishes the contraction rapidly up to a content of 1%, and afterwards

²⁰ *Trans. Amer. Soc. for Steel Testing*, 1922, 3, 279; *J. Iron and Steel Inst.*, 1923, 107, 665.

²¹ *J. Iron and Steel Inst.*, 1923, 107, 139.

²² *Stahl-u. Eisen*, 1923, 43, 713; *J.*, 1923, 779A.

more slowly. Nickel diminishes the contraction very little, with a minimum at about 25%. Chromium diminishes the contraction uniformly to 1·8% at a content of 21·4% Cr.

Castings having a structure of pearlite and graphite have been produced by O. Bauer²³ and these, although only slightly harder than ordinary castings, gave higher bending, tensile, and impact tests and were at the same time readily machinable.

These castings, which are specially suited for parts of steam and internal-combustion engines and machine parts requiring high resistance to wear, are obtained by suitable adjustment of the cupola charge and slow cooling of the casting by the use of a pre-heated mould.

According to F. Wüst and P. Bardenheuer,²⁴ the most important characteristic of semi-steel is the carbon content, which should be between 2·5 and 3·1%. A higher carbon content than this results in the precipitation of too large a quantity of coarse graphite, and a lower content results in a reduction of the tensile strength, unless the silicon and manganese are considerably increased. For small castings, crucible melting is most satisfactory, whilst for large castings the electric furnace gives the most complete desulphurisation and therefore the strongest castings.

The progress made in the manufacture of apparatus in high-silicon iron is shown by A. B. Scorer²⁵ to have been fairly rapid in late years. A short time ago, a simple cascade basin for an acid concentration plant was thought to be a meritorious performance but now, apparatus to be used under onerous conditions, such as centrifugal pumps etc., can be manufactured in acid-resisting material.

With regard to the welding of cast iron, difficulties have been encountered chiefly owing to the junction of the weld being marked by a thin layer of white brittle iron, which is a source of weakness. Lebrun²⁶ has shown how the difficulty may be overcome by the use of grey iron electrodes coated with a mixture containing a large percentage of carbon and preferably also of silicon. When formed in this way, the metal of the weld remains liquid sufficiently long for enough carbon to enter into solution to compensate for that lost by oxidation. Heating of the pieces to be welded, to 600° C., is necessary to prevent the weld metal solidifying too quickly.

The conditions which cause the increase in volume of iron castings during repeated heatings have been studied by J. Durand²⁷ with a view of determining the degree of importance of the various

²³ *Stahl u. Eisen*, 1923, **43**, 553; *J.*, 1923, 722A.

²⁴ *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, 1922, **4**, 125; *J.*, 1923, 835A.

²⁵ *J.*, 1923, 240T.

²⁶ *Rev. Mét.*, 1923, **20**, 248.

²⁷ *Comptes rend.*, 1922, **175**, 522; *J.*, 1922, 899A.

factors affecting it. In the experiments, five cycles of temperature change from 600° to 900° C. were used and the increase in volume was found to become smaller on each successive heating as the amount of free graphite deposited decreased at each stage. As the growth varies inversely with the rate of heating and directly as the silicon content, it is only of importance when the silicon is high and the casting is heated slowly. It follows that stresses will be set up in the material if the temperature varies from one point to another during heating.

An investigation of the process of manufacturing malleable iron castings has been conducted by P. Oberhofer and J. Welter,²⁸ during which the influence of composition, annealing temperature, and oxidising material used on the properties of the malleable castings was studied. With similar annealing conditions, an active oxidising medium, such as haematite, induces a higher impact value than a less active medium, such as mill-scale. Employing a higher annealing temperature when using a moderately active medium with irons of higher sulphur content, enables a further increase of the impact value to be attained, which exceeds that obtained by using a more active medium. Manganese practically neutralises the effect of sulphur and during the annealing this sulphur is not reduced. With higher sulphur, present as iron sulphide, there is a decrease in sulphur content.

The nature of the temper carbon separated from malleable castings has been examined by L. Northcott.²⁹ On comparing the product obtained by separation with natural graphite and lampblack, the following figures were obtained: maximum density, lampblack 1.5, graphite 2.33, temper carbon 2.48. Ignition temperature, lampblack 550°, graphite 670°, temper carbon 650° C. On treatment with potassium chlorate and strong nitric acid, the temper carbon yielded graphitic acid, and it is confirmed beyond doubt that temper carbon is not amorphous carbon, but graphite in a fine state of division.

PROPERTIES OF IRON AND STEEL.

A large amount of investigatory work has been carried out on the preparation and properties of alloy steels, and the effect of the addition of elements not commonly met with in commercial steels is the subject of research in many laboratories. Results obtained by H. W. Gillett and E. L. Mack³⁰ indicate that additions of uranium, boron, titanium, zirconium, and cerium have little effect or do actual harm to the steel, causing inclusions and segregation and showing low and variable recoveries. Molybdenum on

²⁸ *Stahl u. Eisen*, 1923, **43**, 105; *J.*, 1923, 457A.

²⁹ *J. Iron and Steel Inst.*, 1923, **107**, 491; *J.*, 1923, 722A.

³⁰ *Trans. Amer. Electrochem. Soc.*, 1923, **147**; *J.*, 1923, 503A.

the other hand proved to be a true alloying element comparable with nickel, chromium, or vanadium, showing no segregation and giving a quantitative recovery. With the exception of carbon, molybdenum is the most active element used in steel as judged by its influence on the mechanical properties, especially after heat treatment. It increases the depth of penetration of hardening effect so much that many steels containing molybdenum will harden throughout on oil quenching, which without molybdenum would not harden to the centre on quenching in water.

The effect of the addition of carbon and manganese to pure iron has been determined by R. P. Neville and J. R. Cain,³¹ who show that for each 0·01% of carbon up to 0·7%, the ultimate strength of the resulting alloy is increased by 875 lb. to 1150 lb. per sq. in. and the Brinell hardness by 1·8 to 2·6, the effect being greater, the higher the manganese content. By the addition of 1% of carbon, the elongation and reduction of area of pure iron were reduced from 40·5 and 82·5% to little greater than zero, whilst further increases in carbon had little effect on the ductility. For each addition of 0·01% of manganese, the ultimate strength and proportional limit were increased by only about 90–250 lb. per sq. in. and the Brinell hardness by 0·5. Manganese has little effect on the ductility. Further work has been carried out on the effect of manganese additions to carbon steels by H. S. Rawdon and F. Sillers, junr.,³² who find that these additions not only lower the transformation points to a degree corresponding with the proportion of manganese added, but also make the steel less responsive to structural changes than most other elements, which have a similar effect on the critical temperatures. In annealed steels, manganese gives rise to a very fine grained pearlitic or sorbitic structure and in any given steel, addition of manganese results in an increase in the relative proportion of pearlite and a corresponding increase in the Brinell hardness. Manganese additions also cause a reduction in the carbon content of the eutectoid; with 1%, this is reduced to 0·78% C. In rapidly cooled alloys, a decrease in grain size accompanies an increase in manganese content, but no such effect could be detected in the annealed alloys.

The effect of temperature on the mechanical and microscopical properties of low carbon steel (0·16% C), has been investigated by G. C. Priester and O. E. Harder.³³ The results of this work showed maximum values for maximum stress, yield point, and proportional limit at about 300° C., although these values did not exceed the corresponding values at 20° C. As the temperatures at which the

³¹ U.S. Bureau of Standards, *Sci. Paper No. 453, 1922, 18, 411 ; J., 1923, 311A.*

³² *Ibid., No. 464, 1923, 18, 637.*

³³ *Chem. and Met. Eng., 1923, 28, 111 ; J., 1923, 185A.*

tests were carried out increased from 300° to 600° C., the values decreased to an extent corresponding closely to a straight-line function. The alteration in reduction of area and elongation was of a converse order. Increase in the temperature of drawing caused a corresponding increase in the impact toughness and also, above 100° C., in the tensile strength as indicated by impact tests. Changes in the microstructure followed the changes in the mechanical properties in the range 400°–600° C., but no evidence of the maximum and minimum points at 300°, as shown in the mechanical tests, was obtained. The effect of temperature deformation and rate of loading on the tensile properties of low-carbon steel below the thermal critical range has been determined by H. J. French,³⁴ who has found that the maximum ductility occurs in longitudinal tests between 200° and 300° C., but in transverse tests between 150° and 300° C. Cold-rolled steel after heating to 295° C. for a short time showed a decided increase in proportional limit with no change in tensile strength or ductility. The effect of variation in the rate of stress application was studied by means of an apparatus, which photographed simultaneously the indicator readings for stress and strain on a cinematograph film. These show that up to blue heat the tensile properties of steel are independent of the rate of loading, but at 465° C. the tensile strength increased slightly with the rate of loading.

Certain changes which take place in the properties of iron and steel at temperatures below 280° C. have been investigated by F. C. Thompson and E. Whithead.³⁵ For example abnormalities are found in the rate of increase of electrical resistance and of thermo-electric power when used in conjunction with platinum at temperatures of 55°, 100°, 120°, 140°, 220°, and 245°. The changes which occur at 120° and 220° are the most important as they influence the mechanical properties of the metal. It is not considered as probable that the abnormalities are due to allotropic changes. Iron carbide exhibits two well marked abnormalities of a similar nature at 160° and 220° C. It is not clear whether these are distinct points or are the ends of a single transformation range. The electrical resistivities of iron and high-carbon steels quenched from 280° C., are found to be different from those obtained after slow cooling, but when the quenched material is kept at the ordinary temperature, spontaneous tempering takes place, the value of the resistance becoming practically identical with the slowly cooled material after about 12 days.

Among the iron alloys requiring peculiar conditions for successful working, may be mentioned silicon steels containing more than

* U.S. Bureau of Standards, *Tech. Paper No. 219*, 1922, 16, 679; *J., 1923*, 311A.

³⁴ *Proc. Roy. Soc., 1923, A 102*, 587; *J., 1923*, 227A.

4·2% Si. These steels have been investigated by N. B. Pilling,³⁶ who finds that they are too brittle for satisfactory shaping by punching or similar operations and that the brittleness is not permanently removed by heat treatment, but that at a temperature of 100° C. the steels are sufficiently ductile to be worked. Aluminium is found to have a similar effect to silicon.

The increased brittleness of iron which has been galvanised and quenched in the usual way has been shown by W. R. Bean³⁷ to be independent of the zinc coating and due to the presence of phosphorus and silicon in the metal. The exact mechanism of the deterioration has not been determined, but a similar effect is produced by quenching iron which has not been subjected to a molten bath of zinc, the deterioration being intercrystalline.

The danger resulting from the possible inclusion of tinplate scrap in steel furnaces, resulting in the finished steel containing small quantities of tin, is illustrated by results obtained by J. H. Whiteley and A. Braithwaite,³⁸ who have determined the effect of tin on low- and medium-carbon steels. They show that small quantities of tin are liable seriously to impair the ductility, as in steel rails, even 0·06% may be unsafe. The harmful effect of tin apparently increases with the carbon content, for in mild steels the above amount has, apparently, no detrimental effect.

METALLOGRAPHY.

The structure of martensitic carbon steels and the changes in microstructure which occur upon tempering, have been studied by H. S. Rawdon and S. Epstein.³⁹ They show that the coarseness of the martensitic structure depends almost entirely on the quenching temperature and very slightly on the period of heating. Each crystal of austenite is transformed on quenching into a system of martensite needles having a different orientation from neighbouring crystals. The conspicuous martensite crystals are lower in carbon than the filling material, as evidenced by the behaviour of the completely tempered specimens towards etching reagents. The structural changes during tempering below 250° C. are slight, but are shown by the difference in the rate of etching of martensite by alkaline oxidising reagents. Martensite and austenite, if retained, are completely transformed at 250° C., the steel assuming a granular appearance. The scleroscope hardness of the steels decreased very slightly up to 250°, then more rapidly. Increase in the temperature before quenching, or prolonged soaking before quenching, produced

³⁶ Amer. Inst. Min. and Met. Eng., Feb., 1923; *J.*, 1923, 457A.

³⁷ *Ibid.*, Feb., 1923; *J.*, 1923, 458A.

³⁸ *J. Iron and Steel Inst.*, 1923, 107, 161; *J.*, 1923, 508A.

³⁹ U.S. Bureau of Standards, *Sci. Paper No. 452*, 1922, 18, 373; *J.*, 1923,

no marked effect on the hardness of the steels. On the other hand, the uniform cellular martensitic structure of a steel containing C 0·38, Mn 0·52, Si 0·2, Cr 1·08, and Ni 1·87% was not changed at all by tempering up to 704° C., nor was any change noticed by H. B. Pulsifer and O. V. Greene⁴⁰ in the ground mass, grain size, or width of the grain boundaries in this steel, although considerable alteration of the physical properties took place as a result of the treatment. The mechanism of hardening has been further studied by S. Matsushita,⁴¹ who has used a special apparatus for recording the change in length of rods during quenching.

The effect of quenching mild steels containing less than 0·1% C from ordinary hardening temperatures is to show little increase in the hardness number or tensile strength, but M. Sauvageot and H. Delmas⁴² have shown that if quenched from very high temperatures, a considerable increase is shown in both these properties. Bars quenched at 1350° C. showed ferrite and sorbite, at 1400° the transformation to martensite was incomplete, but at 1450° only martensite was present and large crystals had developed. The critical temperature of quenching is known to increase with decrease of carbon, and the same authors⁴³ have shown that this critical temperature reaches the melting point for a steel with a carbon content slightly below 0·09%, the manganese being 0·33%. They conclude from their experiments that the hardening of perfectly pure iron cannot be effected, even at very high temperatures.

An examination of steels containing globular cementite has been made by C. H. Desch and A. T. Roberts,⁴⁴ who show that the maximum strength of the steels falls progressively with advancing conversion of the cementite to the globular form. Various makes of safety-razor blades were examined and were found to consist of minute globules of cementite embedded in an apparently structureless ground mass. It was found that, on heating, solution of the isolated globules of cementite takes place very slowly. The resistance of a blade to wear probably increases with the uniformity and regular distribution of the cementite particles.

N. T. Belaiew⁴⁵ replies to F. Giolitti's⁴⁶ survey of his theory of the secondary structures in steel and points out that the transformation of the dendrites first formed in the solidification of steel into γ -iron involves recrystallisation into independent granules of austenite. The dimensions and distribution of the granules depend on the condition of cooling in the austenitic zone, and while

⁴⁰ *Chem. and Met. Eng.*, 1923, **28**, 354; *J.*, 1923, 312A.

⁴¹ *J. Iron and Steel Inst.*, 1923, **107**, 723; *J.*, 1923, 722A.

⁴² *Comptes rend.*, 1923, **176**, 1146; *J.*, 1923, 554A.

⁴³ *Ibid.*, 1923, **176**, 1310; *J.*, 1923, 607A.

⁴⁴ *J. Iron and Steel Inst.*, 1923, **107**, 249; *J.*, 1923, 723A.

⁴⁵ *Chem. and Met. Eng.*, 1923, **28**, 537; *J.*, 1923, 456A.

⁴⁶ *Ibid.*, 1920, **29**, 585; *J.*, 1920, 410A; *Ann. Reps.*, 1920, **5**, 236.

the general polyhedral structure is produced, the number and distribution of nuclei and subsequently of grains are altered. It is considered that the granulation zone is the true γ -iron zone. The primary conditions for obtaining a well-defined Widmanstätten structure is the development of large grains of austenite in the granulation zone, the subsequent secondary crystallisation being controlled so as to cause the maximum quantity of ferrite to crystallise out along the cleavage planes of the large granules.

The effect on the grain growth of Armco iron, of annealing at temperatures below 650° C., has been studied by L. E. Benson and F. C. Thompson,⁴⁷ who have shown that the grain size increases at a rate depending on the temperature, rapidly during the first few hours, then more slowly, eventually reaching a maximum which is greater the higher the temperature. At 650° the growth stops rather suddenly after five hours and is much less than the maximum attained at 500° . At 800° the growth is much more rapid and is still continuing after 40 hours. Similar results are obtained by annealing low-carbon steels below 700° .

A considerable amount of attention has been given to the occurrence of nitrogen in steel and its effect on the properties etc. A. Fry⁴⁸ considers that iron forms two nitrides, Fe_2N containing 11.1% N and stable up to 400° C., and Fe_4N containing 5.9% N, stable up to 560° C. Above 560° , the latter compound breaks up into a solid solution containing 0.5% N and a eutectoid of Fe_4N and a solid solution containing 1.5% N. On cooling, this becomes magnetic below 480° and it is also magnetic above 740° C.. On treating pure iron with ammonia at 680° C. two nitride layers are formed, the outer one containing more than 8% N and the inner one consisting of twinned crystals of Fe_4N . In the presence of small quantities of carbon, iron that has been treated with ammonia at 600° – 800° C. shows between the outer layer of nitride and the unchanged iron of the interior, a zone of iron-nitrogen eutectoid, braunite. Both the outer and inner nitride layers are much harder than ordinary iron, but both are too brittle to be of practical use. If an alloy steel, containing titanium, chromium, manganese, aluminium, or vanadium, is treated with ammonia just below 580° C., more nitrogen goes into solid solution and an extremely hard outer layer is formed, which renders the metal suitable for making small machine parts, which are subjected to much wear.

The depth of the nitride layer so produced should be about 0.7 mm.; its hardness cannot be increased by quenching and is not reduced by slow heating to 440° C. Above 560° , decomposition of the nitride begins with evolution of nitrogen and a corresponding decrease of hardness.

⁴⁷ *J. Iron and Steel Inst.*, 1923, 107, 525; *J.*, 1923, 554A.

⁴⁸ *Stahl u. Eisen*, 1923, 43, 1271; *J.*, 1923, 1074A.

The influence of nitrogen on steel has also been studied by C. B. Sawyer,⁴⁹ who states that uniform nitrogenisation of iron by heating it in a current of ammonia is difficult, as the hydrogen produced has an effect in the opposite direction. Microscopical examination of treated ingots indicated a solid solution of nitrogen in ferrite up to approximately 0·03% N, nitride needles being observed above this value. Mechanical tests showed a great loss in the ductility of steels containing 0·015–0·03% N. The amount of combined nitrogen in iron and steel has been found by L. Jordan and F. E. Swindells⁵⁰ to increase subsequent to certain heat-treatments in certain cases. An increase of nitrogen was found in the outer layer, but not in the inner layer of an autoclave plate used in the Haber nitrogen fixation process. During an investigation of the methods of determining nitrogen in iron and steel, by F. Wüst and J. Duhr,⁵¹ it was found that the amount of this element varied irregularly in samples of basic Bessemer steel, varying from 0·006% in steel from some works to 0·028% in steel from other works.

A further investigation has been undertaken by F. Wüst⁵² in order to account for these differences, and samples from ten works at various stages in the process have been examined. The results indicate that the quantity of nitrogen taken up increases with the temperature of the bath, and that in all probability a high blast pressure also promotes the taking up of nitrogen.

CORROSION.

The questions of the corrosion of iron and steel, means of reducing or preventing it, properties of stainless steel, etc., have received a large amount of attention and information is being accumulated, which will not only prove immediately useful in the industries, but which will ultimately prove of great importance in the solution of many problems at present imperfectly understood. J. Newton Friend,⁵³ who has made a special study of corrosion, has presented a further report, giving a description of experiments commenced in order to determine by means of "field tests," the relative corrodibilities of various forms of commercial iron and steel under varying conditions of exposure. Simultaneously, laboratory tests have been carried out on the same samples to obtain an indication of their value in practice. The influence of chemical composition, micrographic structure, and other properties upon corrodibility

⁴⁹ Amer. Inst. Min. and Met. Eng., Aug., 1923; *J.*, 1923, 933A.

⁵⁰ U.S. Bureau of Standards, *Sci. Paper* 457, 1922, 18, 499; *J.*, 1923, 312A.

⁵¹ Mitt. Kaiser Wilhelm Inst. Eisenforsch., 1921, 2, 39; *J. Iron and Steel Inst.*, 1922, 105, 650.

⁵² *Ibid.*, 1922, 4, 95; *J. Iron and Steel Inst.*, 1923, 107, 665.

⁵³ *Iron and Steel Inst. Carnegie Scholarship Memoirs*, 1923, 12, 1.

has also been studied. W. H. Hatfield⁵⁴ has published a table which shows whether or not the chief industrial alloys are attacked by various corroding agents, and discusses the results contained therein. Many apparently anomalous results are observed among corrosion phenomena : thus, 5% acetic acid solutions attack a 12–14% chrome steel, whereas vinegar containing 4–5% acetic acid has no effect ; citric acid and lactic acid of all strengths attack the steel, yet neither lemon juice nor sour milk affects it. These and similar results show the importance of examining the behaviour of metals in contact with the exact solutions to which they will be exposed in practice.

Preliminary tests to find a relation between surface tension and corrosion show that corrosion proceeds only when the surface tension of the solution is greater than that of the film. This may account for the difference in action on steel of vinegar and acetic acid of the same strength, the former having a lower surface tension than the latter. W. S. Calcott⁵⁵ has given the following conditions, which should be complied with in order to conduct laboratory corrosion tests from which it is intended to predict the life of a plant constructed of the material under examination : The volume of the solution should be sufficient to render change in composition inappreciable. The temperature should be exactly regulated. The test should be carried on for a sufficiently long time. The test strips should be cleaned with a suitable reagent or a mild abrasive, but not polished. Results are better expressed in diminution of thickness, rather than of weight. The corrosion of steel in sulphuric acid has been studied by W. G. Whitman and collaborators,⁵⁶ who find that corrosion at rest increases with acid concentrations (between 0.0043*N* and 5*N*), though not proportionally. With very dilute acid, corrosion increases with the velocity of rotation ; with stronger acid, it at first falls and then increases, and with a velocity of 12 ft. per sec., the corrosion with acids of all concentrations is the same. The results indicate that corrosion at rest is chiefly corrosion with evolution of hydrogen ; an increased velocity increases the difficulty of forming bubbles and decreases this effect, but it increases corrosion by oxygen depolarisation and this is the predominant effect at high velocities. W. E. Hughes⁵⁷ has pointed out that electrolytic iron, obtained from a solution of ferrous and calcium chlorides, may be more liable to corrosion than iron obtained by the electrolysis of solutions containing ferrous and magnesium sulphates. The difference is attributed to the greater activity of inclusions of chloride impurity in promoting rusting.

⁵⁴ *Trans. Faraday Soc.*, 1923, **19**, 159 ; *J.*, 1923, 1074A.

⁵⁵ *Ind. Eng. Chem.*, 1923, **15**, 677 ; *J.*, 1923, 836A.

⁵⁶ *Ibid.*, 1923, **15**, 672 ; *J.*, 1923, 836A.

⁵⁷ *Chem. and Met. Eng.*, 1923, **29**, 536 ; *J.*, 1923, 1074A.

That the presence of iron sulphide in contact with iron, considerably increases the corrosion of the metal under various conditions is shown by R. Stumper.⁵⁸

The methods employed for the prevention of corrosion of iron and steel are reviewed by B. Zschokke,⁵⁹ and particular attention is paid to the passivity induced by chromic acid and its salts. For practical application in the case of iron structures, it is suggested that the ironwork might be . . . treated with an emulsion of grease and a solution of an alkali chromate, or that a first coat of paint should consist of an emulsion containing a protective solution. It is also recommended that the metal in reinforced concrete work should be covered with a layer of concrete containing a soluble chromate, so that any penetration of moisture through the finishing coat of ordinary concrete should reach the ironwork in the form of a protective solution.

The importance of anticorrosive and antifouling compositions in connexion with shipping is dealt with by P. E. Bowles.⁶⁰ The accepted modern practice is that the vessel must primarily be protected from corrosion and the antifouling composition be applied after the coat of anticorrosive paint. The object of the antifouling coat is the protection against the accumulation of marine life by surrounding the vessel with a solution which is toxic to both animal and vegetable organisms. Of the substances used to render the compositions toxic, salts or compounds of copper and mercury are of first importance, followed by arsenical compounds.

The properties of stainless steel and iron, especially as regards resistance to corrosion, have been further dealt with by J. H. G. Monypenny,⁶¹ who finds that the greatest resistance to corrosion is observed when the steel is in a homogeneous condition obtained by quenching from a temperature sufficiently high to ensure that all carbides are dissolved.

Fully annealed stainless steel is less resistant to corrosion than when in the fully-tempered condition, and when severely distorted, stainless steel rusts comparatively readily. For a given chromium content, the corrodibility is less the lower the carbon present, whilst for a given carbon content, the resistance to corrosion increases with the chromium content.

Ferric chloride and copper chloride solutions attack the steel, but copper sulphate, nitrate, and acetate solutions have no action on it. Atmospheric corrosion and superheated steam are well resisted, as also is sealing up to a temperature of about 825° C. The results of the investigation of the effect of heat treatment on two groups of

⁵⁸ *Comptes rend.*, 1923, **176**, 1316; *J.*, 1923, 607A.

⁵⁹ *Rev. Mét.*, 1923, **20**, 165; *J.*, 1923, 456A.

⁶⁰ *J.*, 1922, 492B.

⁶¹ *Faraday Soc.*, Apr., 1923; *J.*, 1923, 458A.

steels containing 2-12% Cr and 0.35% and 1% C respectively are given by C. R. Austin.⁶² The results given include tensile tests made on the steels annealed at 800°, 850°, and 960° C., also on specimens quenched in oil from 960° and afterwards tempered at 610° or 650° C.

The diffusion of chromium into metals below their melting points is the basis of the chromising patent process. This process is dealt with by F. C. Kelley⁶³ and consists in packing the material to be treated in a mixture of alumina 45% and powdered chromium 55% and heating to a temperature of 1300°-1400° C. in a vacuum or an inert gas such as hydrogen. A suitable furnace for the purpose is made of alundum tubes, wound with molybdenum wire and insulated with alumina. It is necessary that the chromium be in actual contact with the metal in order to be taken up, and a second treatment with fresh contacts must be given if it is desired to increase the penetration of a surface coating. Iron wire treated for 1½ hours showed an increase in weight of 11.7%, diffusion having been effected entirely through the wire. The treated wire was electrically heated in air to 1050° C. for 200 hours without burning out. The product obtained by this process behaves like stainless steel. Nickel may be chromised at a temperature not exceeding 1300° C., but a temperature of 1600° is necessary to effect any penetration into molybdenum or tungsten.

As a means of preventing corrosion, tin-plating is of very great importance, and the chemical problems involved in the tin-plate industry have been dealt with by H. J. Bailey.⁶⁴ This author considers that, although the engineering side of the manufacture has been highly developed, the chemical side is largely carried on by methods handed down from the past without any organised chemical research directed to elucidate the mechanism of the various processes. An outline is given of present practice, and the cause of blisters, hard or thick metal, and the action of flux on the tinning pots, etc., receive attention.

⁶² *J. Iron and Steel Inst.*, 1923, 107, 419; *J.*, 1923, 662A.

⁶³ *Trans. Amer. Electrochem. Soc.*, 1923, 233; *J.*, 1923, 501A.

⁶⁴ *Chem. and Ind.*, 1923, 362.

NON-FERROUS METALS.

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THE general improvement in industrial conditions during 1923 has resulted in an increased demand for many of the common metals, and there have been substantial increases in the prices of lead, zinc, and tin. In Britain the state of trade in the spelter industry, in particular, has improved greatly during the course of the two last years; to a less marked extent tin mining has given rise to more employment consequent upon the re-opening of several of the Cornish mines, brought about not only by the increased value of tin but by the present demand for arsenic. Copper has proved disappointing, and the price, after appreciating in the early part of the year, fell later to the low price prevailing during 1922, thus indicating that the supply more than equalled the demand. The scarcity of platinum, combined with a relatively large demand, has resulted in a considerable increase in value, which is likely to be maintained until more settled conditions in Russia permit of an extended development of the deposits in the Urals. Silver has not enjoyed a good market during the year.

No very important developments in the form of new metallurgical processes appear to have taken place during 1923, though it is possible that some of the large-scale experiments carried out by the U.S. Bureau of Mines may lead to striking improvements in some processes in the near future.

PROCESSES OF ORE CONCENTRATION.

H. M. Roche¹ gives an account of the new magnetic concentration mill at the Richard iron mine, New Jersey, operating on non-Bessemer magnetite, containing 65–15% of iron, with details of the preliminary crushing and the stages of magnetic concentration for sized grades of material. Coarse ore, + 8-mesh, is treated in the Ball Norton dry drum type while fines – 8-mesh are treated in the Roche wet belt machine. The wet belt machine consists of a set of magnets underneath an inclined vanner or flanged belt; the machine is set at an angle of 10°–80°, the belt

¹ *Eng. and Min. J. Press*, 115, 923.

moving up the incline towards the headwheel and the feed mixed with water being fed to the lower magnets. The magnets are of the alternating-pole type, and twenty magnets, spaced 3-inch centres, are used in each machine. The feed strikes the magnets near the footwheel, and the magnetic iron material clings to the belt and is carried over the upper magnets and head wheel while the tailing is washed down over the footwheel. As the ore travels up the belt, wash water is added, and as the ore passes from one pole to another a loop $\frac{1}{2}$ - $\frac{3}{4}$ inch high is formed, the magnetic particles turning over in looping. Strong currents of wash water coming down the belt wash through the loops of ore and remove the non-magnetic material. The tailing assays about 2·2% Fe, and the recovery amounts to 99%.

A. H. Parsons² describes the use and advantages of rubber linings in tube and ball mills at Nipissing, and states that output is increased and costs are lowered.

G. J. Young³ outlines the selective flotation of a complex zinc-lead ore of the following composition:— Lead, 10–11%; zinc, 12–13%; silver, 3 oz. per ton; sulphur, 30–32%; and iron, 32–33%. The ore is ground, so that 95% passes through a 200-mesh sieve, in strongly alkaline water, and the galena is separated in a 1:1 pulp at a temperature of 22°–24° C.; a 1:1 mixture of water-gas tar and coal tar creosote is the flotation agent used. Copper sulphate and water-gas tar are added in the second flotation machine and the blende is separated from the iron sulphide and gangue. Lead concentrates containing 60% of lead and about 7% each of zinc and iron, and zinc concentrates containing over 40% of zinc are obtained.

A. W. Hahn⁴ gives an account of patents issued to C. M. Nokes and R. V. Smith covering the use of a combination of paraffin and sodium sulphide in the flotation process when applied particularly to oxidised copper ores, refractory manganese silver ores, and oxidised gold ores. Satisfactory results were obtained in a test mill having a capacity of 20 tons of ore daily.

•THE METALLURGY OF COPPER, NICKEL, AND ARSENIC.

In 1923, as in 1922, progress in the extraction of copper from its ores has been made chiefly in the direction of hydro-metallurgical treatment. A. W. Allen⁵ gives an illustrated account of modern leaching processes for the treatment of copper ores and Chilean nitrate pampa. He emphasises that the efficient extraction

² Eng. and Min. J. Press, 116, 289.

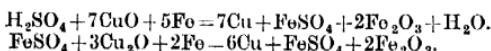
³ Ibid., 116, 453.

⁴ Min. and Met., 1923, 4, 485.

⁵ Chem. and Met. Eng., 1923, 29, 671.

of soluble material associated with an insoluble gangue depends primarily on correct physical conditions. Reduction in particle size may not lead to better results, and there is an economic limit to the degree of crushing that should be practised. Comparatively coarse crushing may show a higher extraction than finer crushing, because even percolation of the solution is possible around all the particles, resulting in an even displacement.

An abstracted account of the Neville-Soanes process⁶ states that it consists of agitating oxidised and roasted ore with sulphuric acid or ferrous sulphate and finely divided iron at 70° C. The consumption of iron is much less than in ordinary processes, only $\frac{1}{2}$ lb. of iron being required to precipitate 1 lb. copper in the case of average ores; with slimes the operation is of only a few minutes' duration, and the copper is subsequently floated. The following reactions are typical of those supposed to take place:—



H. S. Mackay,⁷ in describing the Mackay electro-chemical process for the treatment of copper ores, gives reasons for the failure of early processes. His own process differs from others of the same class in that little or no impurity can accumulate in the solvent of the electrolyte, and it does not need to be supported by the addition of chemicals. Advantage is taken of the fact that by carefully controlled roasting iron sulphate can be formed and subsequently decomposed to oxides without converting an appreciable proportion of the formed copper sulphate into the insoluble condition. Subsequent leaching with dilute sulphuric acid yields in consequence a fairly pure copper sulphate solution with only small quantities of iron and other salts. Electrolysis of the leached solution becomes highly efficient, and in this operation the solvent becomes regenerated. When the small quantity of soluble iron accumulates to the extent of about 0·5% the current efficiency is reduced about 8%, so the electrolyte is agitated in the presence of air with fine roasted ore by means of which the iron is precipitated. A plant is to be built in Australia to treat per day 500 tons of silicious ore containing 4% of copper.

F. Laist⁸ gives his views with regard to the ideal copper smelter and deals with the general lay-out of the plant. His opinion is that the only type of roasting furnace to be considered nowadays is the multiple-hearth furnace of the MacDougal type. Its advantages over other forms are simplicity of mechanical design,

⁶ Eng. and Min. J. Press, 116, 193.

⁷ Ibid., 116, 975.

⁸ Min. and Met., 1923, 4, 243.

low repair costs, and excellent conservation of heat. Its chief disadvantage is the large amount of dust it produces; this can, however, be readily recovered in a Cottrell plant. He discusses the firing of reverberatory furnaces, and states that they are now heated by either coal dust or oil, the old practice of grate-firing having been almost entirely superseded. The choice of the method of firing will depend largely on the cost of the method adopted. Both upright and horizontal converters have been found satisfactory, but under most conditions the author thinks the horizontal type preferable.

W. A. Heywood,⁹ in a paper on the selection of a copper smelting plant, discusses the relative merits of reverberatory and blast furnaces with regard to installation costs, operation, and fuel consumption, and decides generally in favour of the blast furnace as being the cheaper melting agent.

E. K. Judd¹⁰ gives an interesting account of a modern copper smelting plant, the "New Oroya" smelter of the Cerro de Pasco Copper Corporation, designed to smelt 2500 tons of ore per day. Details of the initial and fine crushing plant, methods of transporting and distributing materials, coal pulverising plant, and coal blowing system for the reverberatory furnaces are given. The roasting plant consists of ten $22\frac{1}{2}$ ft. seven-hearth Wedge furnaces, and each roaster has its own Cottrell precipitating unit of 146 tubes. The sintering equipment consists of ten standard type Dwight-Lloyd machines. Two 25-ft. \times 100-ft. reverberatory furnaces, and two blast furnaces 60 ins. wide \times 40 ft. long inside in the plane of the tuyères are used for the production of matte, which is subsequently blown in five Pierce-Smith converters of dimensions 12 ft. \times 20 ft.

G. J. Young¹¹ describes lead and copper smelting practice, the electrolytic zinc plant, and the refining of base bullion and copper at the Trail smelter.

C. B. Carpenter and C. R. Hayward¹² publish an account of their research on the equilibrium diagram of the system Cu₂S-FeS. They found the sulphides to be completely soluble in one another when liquid, but only partly soluble when solid, the two branches of the liquidus curve intersecting at a point below the freezing-points of the pure constituents. The eutectic range extended from approximately 92.5% FeS to 50% FeS, the pure eutectic containing about 68% FeS. A transformation occurs between the same limits in the solid state at 950° C., but there was no

⁹ *Trans. Inst. Min. and Met.*, Apr., 1923.

¹⁰ *Min. and Met.*, 1923, 4, 499.

¹¹ *Eng. and Min. J. Press*, 116, 453.

¹² *Ibid.*, 115, 1055.

evidence of transformations at lower temperatures nor of the presence of chemical compounds. With compositions ranging between 45% FeS and 15% FeS the charge swells on cooling and metallic copper separates. It was found that the separation of copper occurred most readily in the mixtures which had been heated in the molten condition to relatively high temperatures, e.g., 1260° C., and the authors suggest that FeS loses some sulphur by volatilisation and that on subsequent cooling the reaction $\text{Fe} + \text{Cu}_2\text{S} = 2\text{Cu} + \text{FeS}$ takes place. In melts containing more than 45% FeS the free iron liberated remains dissolved in excess FeS and does not react. The arrest at 950° C. is said to be due to a change in the crystal habit of Cu_2S . This explanation does not appear to be satisfactory, as there is no indication of an arrest in melts rich in Cu_2S but only in melts containing eutectic. A critical examination of the liquidus on the copper side of the eutectic range indicates that there is room for further study, especially in the region about 50% Cu_2S , where a compound may exist. The solidus lines were not carefully studied, and the photo-micrographs reproduced are not so clearly understood as the text indicates.

R. S. McBride¹³ gives an interesting account of a new plant of the International Nickel Co. for the production of malleable nickel and Monel metal. The production of Monel metal from matte is described; final reduction of the oxides with charcoal is effected in acid open-hearth furnaces, or, for special charges low in sulphur, in basic-lined electric furnaces. One oz. of magnesium is added for the de-oxidation of 100 lb. of metal prior to casting into ingots weighing two tons each, including a sink head of about 25%. The ingots are cleaned by milling and chiselling, re-heated, and hot forged to billets, which are then rolled.

Calcium arsenate has proved to be the most effective agent for controlling the boll weevil, and a very large demand for it has arisen. An article on "Developments in the production of arsenic at Anaconda"¹⁴ is consequently of special interest. Butte ores average 0.5% As_2O_3 , and the flue dusts from the roaster gases contain from 7.5 to 17.5% As_2O_3 , while the dust from the Cottrell plant contains 25-35% As_2O_3 . These gases are passed through Cottrell treaters to give a product assaying 70-85% As_2O_3 . After re-treatment of the dust (diluted) in a reverberatory furnace a condensed crude arsenic, over 90% As_2O_3 , is obtained and sent to the refining plant, which consists of two reverberatory refining furnaces in which the As_2O_3 is melted and volatilised, the vapours passing through chambers to a bag house.

¹³ *Chem. and Met. Eng.*, 1923, 29, 745.

¹⁴ *Min. and Met.*, 1923, 4, 385.

METALLURGY OF ZINC AND LEAD.

W. Kapellman¹⁵ gives a description of the Fiechtl vertical retort for zinc ores, which consists of a double row of vertical retorts arranged within the furnace and parallel to its length. This facilitates charging by means of the charging car above and also the removal of the ashes by the ash car below. The lower end of each retort is closed by means of a cone-shaped valve bottom, which is raised or lowered by a handwheel. Zinc is condensed in the usual manner. By comparison with the Belgian retort process the cost of installation is reduced 40%, fuel by 27%, and labour 70%.

J. D. Hannah and E. L. Rhead¹⁶ give the results of experiments which show the beneficial effect of the addition of lead in the promotion of the formation of spangle. Up to 3% of tin or aluminium fails to produce any improvement in spangle. The authors explain the influence of lead as being due to the dispersion of drops of lead in the zinc bath owing to the formation of conjugate solutions. "Added lead or bismuth is segregated in definite areas of the coating, and this segregation forms the essential mechanism of spangling."

A publication¹⁷ issued by the U.S. Bureau of Mines on "Chloride volatilisation process of ore treatment" states that efficient chloridising and volatilisation of copper, silver, gold, and lead may be obtained by roasting the ore with sodium or calcium chlorides or their mixtures in shallow layers in a rotating tube furnace and collecting the fume in a Cottrell precipitator. In small-scale tests very good extractions were obtained from many complex ores. The furnace was maintained at a temperature of 950°-1000° C. during the process. Lead is the most readily chloridised metal and is followed by copper; silver gives rather erratic results, which are influenced by the moisture present, and zinc is very difficult to volatilise.

O. C. Ralston¹⁸ shows that oxidised lead compounds, cuprous chloride, and silver chloride are appreciably soluble in hot brine solutions. The process he describes should be suitable for the treatment of tailings from hydro-metallurgical zinc extraction plants, flue dusts, etc. After leaching, a variety of methods of precipitation, electrolytic and chemical, have proved satisfactory.

It would appear that in the near future applications of wet methods to the treatment of lead ores will become increasingly important.

¹⁵ Eng. and Min. J. Press, 114, 1153.

¹⁶ J. Inst. Metals, 1923, 30, 79; J., 1923, 980A.

¹⁷ T. Varley, E. P. Barrett, C. C. Stevenson, and R. H. Bradford, Bull. 211, 1923; J., 1923, 724A.

¹⁸ Min. and Met., 1923, 4, 625 (Abstract).

METALLURGY OF THE PRECIOUS METALS.

A. H. W. Cleave¹⁹ describes an improvement in electrolytic silver refining practised at the Royal Mint, Ottawa. The silver is deposited with a current density of 75-150 amps. per sq. ft. on rotating cathodes running at a peripheral speed of 40 ft. per minute in circular cells 36 ins. in diameter.

The refining of gold bullion with chlorine²⁰ at the same mint is described and some details of the process are given, but they do not appear novel.

D. L. H. Forbes²¹ gives an account of the use of sodium peroxide in cyanidation at the Teck-Hughes gold mine, where the gold is partly in combination with tellurium. The addition of sodium peroxide to the pulp to the extent of up to 1 lb. or more per ton of ore was found to increase the extraction. An ore of \$20-30 grade gave good results with an addition of peroxide of 0·4-0·6 lb. per ton; the increased milling cost was 12-18 cents per ton, whereas the increased recovery amounted to 50 c.- \$1 per ton.

H. B. Wright,²² in a paper entitled "The regeneration of cyanide solutions," outlines the treatment of gold residue dumps at the Mitchell's Creek gold mine, N.S.W. The material contained as cyanicides, copper, lead, and bismuth in sufficient quantities to render the ordinary direct cyanide method impracticable owing to the high consumption of cyanide. Sands were treated with fresh and regenerated cyanide solutions, and the gold was precipitated in zinc boxes. Solutions free from active cyanides and alkalis were treated with sulphuric acid, of which 380-700 lb. was used for 50 tons of solution. Copper was precipitated as cuprous cyanide, which was allowed to settle and the clear solution decanted. Milk of lime was subsequently added and stirred into the solution to fix the hydrocyanic acid and give an excess of about 0·1% of lime. The regenerated solution was used for mixing with fresh solutions and as washes following strong solutions. The cuprous cyanide was collected, dried, and roasted to copper oxide. The remarkable statement is made that 80% of the gold and silver can be precipitated with the cuprous cyanide by the addition of sulphuric acid.

A considerable reduction in zinc consumption²³ and an increase in the bullion content of the precipitate is effected from deoxidising the cyanide solutions before zinc precipitation. To insure the best precipitation the solutions should be rich in cyanides.

¹⁹ Eng. and Min. J. Press, 116, 21.

²⁰ Ibid., 116, 236.

²¹ Ibid., 115, 440.

²² Ibid., 115, 806.

²³ Ibid., 115, 117.

R. S. Butsford²⁴ gives an account of the occurrence of platinum in the Urals and of the washing and dredging methods of extraction ; he forecasts the future extension of the mining area.

METALLOGRAPHY.

*Metallographical Standards.*²⁵—Tentative standards, definitions, practices, etc., were recently published for criticism by the American Society for Testing Materials. Definitions of terms, the technique of photomicrography, the preparation of various metals and alloys, and etching reagents are dealt with.

A. Portevin²⁶ presents an excellently illustrated paper on "Corrosion figures in microscopic metallography." Etching reagents which act by the solution or corrosion of the polished surface reveal the crystal structure—that is, the constituent grains of the phases—on account of two related phenomena, characteristic of the material in the crystallised condition : (1) Inequality of the rate of solution, a function of the crystalline orientation of the plane attacked, which gives rise to ridges between the etched sections of adjacent grains showing in relief the boundaries which throw shadows under oblique illumination. (2) The birth of corrosion figures which are the origin of the variation in brilliancy existing between adjacent grains. (a) The symmetry of these figures is similar to that of the particular crystal or grain ; (b) the form, number, development, and clearness of the corrosion figures depend on the etching conditions, that is, on the nature and concentration of the etching reagent, and the time and temperature of the attack.

J. Strauss²⁷ recommends the use of hydrofluoric acid preliminary to the use of more ordinary etching reagents for aluminium bronze.

A. M. Portevin²⁸ contributes a lengthy and well-illustrated paper on "The structure of eutectics," and discusses the morphology of the eutectic and the genesis of the eutectic structure ; the influence of surface tension, surfusion, the pro-eutectic constituent and other matters are considered, and an appendix deals with the deformation, recrystallisation, and hardness of eutectics. The rareness of the lamellar type of eutectic is pointed out.

Equilibrium in the system of gold-zinc is dealt with by P. Soldau,²⁹ who studied the system by the measurement of electrical conductivity at various temperatures, by thermal analysis and microscopic structure. He found evidence of the existence of the intermetallic compounds Au_3Zn , AuZn , and AuZn_3 .

²⁴ *Min. and Met.*, 1923, **4**, 595.

²⁵ *Metal Ind.*, 1923, 480, 510.

²⁶ *Rev. Mét.*, 1923, **20**, 381.

²⁷ *Chem. and Met. Eng.*, 1923, **28**, 852.

²⁸ *J. Inst. Metals*, 1923, **29**, 239.

²⁹ *Ibid.*, 1923, **30**, 351.

PHYSICAL AND MECHANICAL PROPERTIES.

Z. Jeffries and R. S. Archer³⁰ discuss at length the properties of cold-worked metals. They state that while the general effects of cold working are an increase in hardness and loss of plasticity various specific properties are affected in somewhat different ways. The yield point is probably affected by cold working more than any other property of the hardness group; thus the yield point of iron (in wire) is raised by cold work to a value practically identical with the raised tenacity. In general, the increase in hardness and loss in plasticity are continuous with increasing amounts of cold work. The rate of change tends to decrease as the amount of work becomes large. The conditions at the slip planes are discussed in a characteristically interesting fashion, but at too great length to be satisfactorily summarised in a few lines. The authors conclude with a suggestion of the cause of strain hardening. Since the resistance to motion along a slip plane may be greater than in the unbroken crystal, these slip planes are sources of strength and hardness aside from the slip interference action. The hardening effect of deformation increases with the number of slips taking place.

The same authors, in a paper on "The modern concept of solid solutions,"³¹ make a contribution embracing recent ideas on the subject under headings dealing with solvent and solute, limited solubility and its variation with temperature, solidification and melting of solid solutions, annealing temperatures, density of solid solutions, electrical conductivity, coefficient of resistance, hardness, strength and ductility.

E. C. Bain³² discusses the nature of solid solutions and considers the change in space lattice in binary systems of a number of metals which form continuous series of solid solutions. The stretching of the space lattice is not generally so great as would be expected from a proportional increase in lattice size computed from atomic volume considerations. This indicates a weak but perfectly definite attraction between unlike atoms. In a later paper³³ Bain states that in the lattice structure of cored crystals, characteristic spotted patterns of large grains are not obtained, but, instead, the well-marked spectrogram of smaller grains further modified by what must be a mixture of space lattices of various sizes. "When the mechanism of coring is analysed we come to the conclusion that the resultant alloys are actually an assortment of many crystals of varied spacings. The apparent grain boundaries enclose several orientations."

³⁰ *Chem. and Met. Eng.*, 1922, **27**, 882.

³¹ *Ibid.*, 1923, **29**, 923, 966.

³² *Ibid.*, 1923, **28**, 21.

³³ *Ibid.*, 1923, **28**, 65; *J.*, 1923, 230A.

H. I. Coe,³⁴ who carried out compression tests on small cylinders of metals, found that with successive increments of loads plastic flow occurred, after the elastic limit had been exceeded, at an increasing rate. Graphical representation showed that at a certain load the rate of flow for a given increment of load undergoes a more or less abrupt change, very soft metals such as tin and lead becoming perfectly plastic, and harder metals becoming more plastic than under preceding loads and immediately succeeding loads. When this particular load was expressed as a stress per sq. in. of the enlarged section of the cylinder, it was found that the value obtained agreed very closely with the maximum load per sq. in. in tension of the same material. The term "critical plasticity" is used to indicate the change in the rate of plastic deformation which most metals exhibit at a particular load. Annealed metals appeared to commence flowing at a comparatively low load and continued doing so at an increasing rate up to the load corresponding to critical plasticity; the same metals, however, in the worked condition were much more resistant to compressive stresses until they approached near the load corresponding to critical plasticity, when they suddenly collapsed and a marked temporary flow occurred.

H. C. H. Carpenter and C. C. Smith³⁵ give an account of tests carried out on work-hardened aluminium sheet. The loss of work-hardness, measured by the tenacity, after annealing at temperatures up to 200° C. for long periods, measured in years, was determined. Up to 75° C. the retention of work-hardness was practically complete; annealing for 2·46 years at 200° C. gave a loss equal to 66%. The differences in the rate of loss of work-hardness for different thicknesses of sheet were not large, but they tended to be larger the greater the amount of work done on the sheet. The purer the aluminium the more the retention of work-hardness on annealing.

J. Czochralski³⁶ states that at temperatures above 1300° C. aluminium in contact with carbonaceous materials absorbs small quantities of carbon to form the carbide Al_4C_3 , which on solidification forms small plates. Commercial aluminium was found to be practically free from sodium. The relationship with other metals is also considered.

K. E. Bingham and J. L. Haughton³⁷ record the results of their investigation of the equilibrium conditions of aluminium alloys containing up to 12% of copper and 10% of nickel. Thermal analysis was carried out with special arrangements to prevent

³⁴ *J. Inst. Metals*, 1923, 20, 309; *J.*, 1923, 984A.

³⁵ *Ibid.*, 1923, 29, 29; *J.*, 1923, 358A.

³⁶ *Z. Metallk.*, 1923, 15, 273; *J.*, 1923, 1226A.

³⁷ *J. Inst. Metals*, 1923, 29, 71; *J.*, 1923, 358A.

segregation. Difficulties arose in the measurement of electrical resistance due to partial or complete loss of contact between leads and specimen owing to the formation of a film of oxide on the aluminium. A thorough microscopical examination was made and details of the methods of polishing and etching are given. The constitutional diagrams that are reproduced are of a complex character.

D. Hanson and M. L. V. Gayler³⁸ deal with the heat treatment and mechanical properties of aluminium with small percentages of copper, and from the results of tensile and hardness tests conclude that copper-aluminium alloys containing up to 2% of copper are not appreciably affected by quenching from 500° C. and subsequent age-hardening. Alloys containing from 2·5% to 5% of copper are profoundly affected by this form of heat treatment. The strength of a rolled and annealed 5% alloy is increased from 12 tons per sq. in. to 23 tons as a result of quenching and ageing; at the same time the elongation remains high.

In a paper on "The production and heat treatment of chill-castings in aluminium alloy ('Y')," W. Rosenhain, S. L. Archbutt, and S. A. E. Wells³⁹ remark on the widely varying tensile properties found. On a number of unsatisfactory test pieces of heat-treated "Y" alloy slightly discoloured spots were visible on the fracture; fractures of bars tested "as cast" did not show the spots, which were found to be due to heat treatment. The conclusion was drawn that the discoloured patches observed on the fractures of bars as ordinarily heat treated are due to the penetration of oxidising gases through the metal into cavities existing in the cast bar. Density determinations showed that unsoundness was located at or near the centre of the bar. For a one-inch diameter bar and a specified iron mould, a mould temperature of 350° C., and a casting temperature of 750° C., were found the best. A study of different iron moulds with different ratios of cross-sectional areas of mould to casting indicated a ratio of 3 : 1 as being most suitable with a mould temperature of 150°-200° C. Too severe a chilling of the metal by the mould results in the formation of too deep a ring of chill crystals radiating inward from the surface of contact with the mould, and is accompanied by sponginess of the centre of the bar and general weakness.

M. L. V. Gayler⁴⁰ deals with the constitution and age-hardening of certain ternary and quaternary alloys of aluminium.

L. Guillet⁴¹ describes the results of experiments on special aluminium bronzes (copper-aluminium-nickel). He determined the

³⁸ *J. Inst. Metals*, 1923, **29**, 491; *J.*, 1923, 358A.

³⁹ *Ibid.*, 1923, **29**, 191; *J.*, 1923, 358A.

⁴⁰ *Ibid.*, 1923, **29**, 507; 1923, **30**, 139; *J.*, 1923, 359A, 981A.

⁴¹ *Rev. Met.*, 1923, **20**, 130; *J.*, 1923, 313A.

coefficient of equivalence of silicon, manganese,⁴² iron, and nickel relative to aluminium in aluminium bronzes in a manner similar to his well-known determination of the equivalence of elements as regards zinc in the brasses. Important results of mechanical tests on cast alloys showing the influence of nickel on aluminium bronzes containing respectively 90, 83, 75, and 60% of copper are given. Small quantities, up to about 5% of nickel, in general have no very marked effect, but larger quantities raise the maximum stress and elastic limit, whilst the ductility, as measured by elongation, is lowered. The microstructure of the alloys is dealt with briefly and some reference is made to the influence of mechanical and thermal treatment. The same author⁴² discusses the effect of phosphorus, magnesium, and cobalt on the properties of aluminium bronze. The influence of phosphorus to the extent of 0·2% was found to be very harmful, both the ultimate stress and the elongation being reduced. Magnesium embrittles the alloy, and it appeared that cobalt possessed no beneficial influence; in fact, it seemed to be actually harmful.

J. D. Edwards⁴³ has made density measurements of cold and hot aluminium-silicon alloys containing up to 15% of silicon, and found that crystallisation shrinkage decreases with increasing amounts of silicon.

C. R. Austin and A. J. Murphy⁴⁴ record an extensive research into the liquidus and solidus over the whole range of the copper-aluminium-nickel system of alloys. The compound NiAl possesses the high melting point of 1640° C.

H. O'Neill⁴⁵ found that indentation tests on single crystals of aluminium indicate that the rhombic-dodecahedral face has the greatest mean hardness, 23·3; the octahedral face is softer, 21·3, and appears to be slightly harder than the cube face. The presence of grain boundaries in aluminium does not appreciably affect the resistance of the metal to indentation.

A. L. Norbury,⁴⁶ in investigating the hardness of annealed copper, sought to obtain a more definite expression for the Brinell hardness. A definite expression for the hardness of copper must take into account the annealing temperature, or some factor which is being influenced by the annealing temperature.

In another paper Norbury⁴⁷ measures the hardnesses of certain copper-rich α -solid solutions in order to compare the relative effects of different elements in increasing the hardness of copper. In a contribution on "Some experiments on the hardness and

⁴² *Rev. Mét.*, 1923, **20**, 257; *J.*, 1923, 555A.

⁴³ *Chem. and Met. Eng.*, 1923, **28**, 165; *J.*, 1923, 228A.

⁴⁴ *J. Inst. Metals*, 1923, **29**, 327; *J.*, 1923, 357A.

⁴⁵ *Ibid.*, 1923, **30**, 299; *J.*, 1923, 981A.

⁴⁶ *Ibid.*, 1923, **29**, 407; *J.*, 1923, 356A.

⁴⁷ *Ibid.*, 1923, **29**, 423; *J.*, 1923, 357A.

spontaneous annealing of lead⁴⁸ the same author described an ingenious adaptation of a lever tensile testing machine for making low-load Brinell impressions. Brinell hardness tests were made on lead using various loads, maintained for various lengths of time, and the results were interpreted according to Meyer's formula $L = ad^n$. The effect of cold-hammering was to increase the hardness; the spontaneous annealing of lead was studied, and it was found (1) that, within certain limits, the greater the amount of cold work the greater the hardening; (2) that lead spontaneously anneals at room temperatures; (3) that the rate of annealing increases with the amount of deformation. It was observed that lead which had been very severely hammered became dead soft within 20 seconds.

L. Aitchison⁴⁹ in describing the mechanical properties of magnesium alloys, gives an account of mechanical tests on Electron metal and alloys of magnesium with, respectively, 1% of cadmium, 6% of aluminium, 11% of aluminium, 3% of copper, and 13% of copper, and comes to the conclusion that it is doubtful whether, for the purposes of the aircraft engineer, the alloys are really effectively light, in view of their low elasticity and not uniformly good mechanical properties. Better properties in the magnesium alloys may follow from further development. H. J. Maybrey, in the discussion of the paper, stated that good results had been obtained by the Magnesium Co. after prolonged experiments in the production of good castings.

D. Hanson, C. Marryatt, and G. W. Ford⁵⁰ give the results of an important investigation into the effect of oxygen on copper. Considerable difficulty was encountered in the production of sound castings and complete success was not attained. The oxygen content of the castings ranged from 0·015 to 0·36%. It was concluded that oxygen has a relatively small effect on the properties of copper, and is neither seriously deleterious nor markedly beneficial. The mechanical properties are not much affected by small quantities of oxygen, and a metal containing as much as 0·1% differs very slightly from pure copper. The electrical conductivity does not fall very much, and values exceeding 100% of the International Standard are obtained in all annealed material containing less than 0·1% of oxygen. The small effect of oxygen is probably due to its extremely low solubility. The authors emphasise that their conclusions are applicable strictly only to pure copper containing oxygen and free from other impurities, and that the present research is a basis for other work.

⁴⁸ *Trans. Faraday Soc.*, 1923, **19**, 140.

⁴⁹ *J. Inst. Metals*, 1923, **29**, 17; *J.*, 1923, 359A.

⁵⁰ *Ibid.*, 1923, **30**, 197; *J.*, 1923, 980A.

D. H. Ingall⁵¹ has published a paper entitled "Experiments with copper wire : cohesion a function of both temperature and cold work." He determined for a number of loads, the temperature at which wire broke under a given load. The temperature-load curves reproduced show an inflection at 350° C., and the low-temperature straight line portion of the curve conforms to the ordinary algebraical equation $y = a + bx$ where y is the tensile stress, x the temperature, and a and b are constants. The value a represents a relative measure of the susceptibility of the material to hardening or strengthening by cold work, and b the susceptibility to softening or annealing with rise of temperature. The high-temperature portion of the curve corresponds to the equation $xy^n = k$, where n and k are constants, and either x or y may be cohesion or temperature as the case may be. Values for n and $\log. k$ are given for the various series of experiments. It is established that beyond 350° C. the cohesion or tensile strength of the copper used is a function of both temperature and work up to 50% reduction.

According to M. Cook,⁵² recrystallisation of cold-worked cadmium occurs between 50° and 60° C., the greater the reduction the lower being the temperature. D. Hanson criticised the work on the ground that sufficient attention had not been paid to an allotropic change occurring at 60° C.

W. Fraenkel and H. Becker,⁵³ in dealing with the kinetics of the transformation of quenched $\alpha\beta$ -brass, point out the changes in structure of homogeneous β in quenched 60 : 40 brass on annealing between 150° and 200° C.; a fall in the electrical resistance was observed.

Experiments were carried out by R. C. Reader⁵⁴ on some properties of the copper-rich aluminium-copper alloys, who studied the density volume changes and heat treatment of alloys containing up to 11% of aluminium. Maximum ductility was obtained in a 10% alloy by annealing for short periods at 700° C. after quenching from 900° C.; a very fine $\alpha + \beta$ structure, indicative of strength and ductility, is imparted to the alloy.

H. Heape⁵⁵ finds that for cast alloys of copper with tin, in general, hardness varies in the same order with the density.

According to A. H. Mundey and C. C. Bissett,⁵⁶ no substantial advantages accompany the use of 1% of nickel in high-grade bearing metal; in fact, some valuable properties are diminished. Nickel appears to have the effect of suppressing the network of the

⁵¹ *J. Inst. Metals*, 1923, **30**, 171; *J.*, 1923, 981A.

⁵² *Ibid.*, 1923, **29**, 119; *J.*, 1923, 360A.

⁵³ *Z. Metallk.*, 1923, **15**, 103; *J.*, 1923, 555A.

⁵⁴ *J. Inst. Metals*, 1923, **29**, 297; *J.*, 1923, 358A.

⁵⁵ *Ibid.*, 1923, **29**, 467; *J.*, 1923, 357A.

⁵⁶ *Ibid.*, 1923, **30**, 115; *J.*, 1923, 983A.

copper-tin constituent, which has been shown to be of value in reducing segregation in tin-rich bearing metals.

Calcium-lead bearing metals are discussed by L. Filipoff,⁵⁷ who gives an account of the properties and microstructure of a bearing metal containing 1·9% of calcium, 1·00% of strontium, 1·10% of barium, 1·37% of copper, 0·10% of sodium, the remainder being lead, and compares them with those of the ordinary tin-rich bearing metals. Except for their liability to oxidation during melting, the author considers the alkaline-earth bearing metals superior to those containing tin, which possess the disadvantage of having a relatively low melting point.

W. Guertler⁵⁸ deals with the properties of alloys of molybdenum with tungsten, tantalum, platinum, palladium, chromium, iron, nickel, cobalt, and copper, and finds that with a high proportion of molybdenum the alloys are usually hard and brittle.

L. Guillet and M. Ballay⁵⁹ conclude, from the results of their experiments on the influence of work on the resistivity of metals and alloys, that the resistivity of pure worked metals is slightly changed by annealing; the differences are below 4%. Annealing decreased the resistivity of all the metals experimented with, except tin and lead, for which a slight increase was observed. On the other hand, the resistivity of certain alloys is considerably changed by annealing, alloys consisting of a solid solution showing the greatest change. For most alloys the resistivity of the worked material is lowered by annealing, though the contrary holds for German silver.

A. W. Gray⁶⁰ gives a large amount of valuable information on the volume changes accompanying solution, chemical combination, and crystallisation in amalgams. The general curve of reaction-expansion of silver-tin-copper amalgams is characterised by four consecutive stages of alternate contraction and expansion; an explanation of a typical curve is given. Factors that influence dimensional changes, such as fineness of alloy, trituration, etc., are considered, and a considerable amount of experimental data is given.

R. C. Reader⁶¹ finds that pure metals which solidify at a constant temperature are not affected as regards density by the rate at which they solidify. Alloys which solidify over a range of temperature give a lower density in the interior of the bar when chill cast, while other alloys are not so affected. The very interesting fact was established that alloys that solidify through

⁵⁷ *Metal Industry*, 1923, 145.

⁵⁸ *Z. Metallk.*, 1923, 15, 150, 251; *J.*, 1923, 1075A.

⁵⁹ *Rev. Mét.*, 1923, 20, 398; *J.*, 1923, 781A.

⁶⁰ *J. Inst. Metals*, 1923, 29, 139; *J.*, 1923, 359A.

⁶¹ *Ibid.*, 1923, 20, 105; *J.*, 1923, 983A.

range of temperature are inversely segregated on rapid solidification; that is, they are richer on the outside in the component of low melting point and richer in the centre in the component of high melting point.

With the use of a thermo-balance H. Endo⁶² determined the volume changes during the melting of ice, mercury, sodium, tin, bismuth, thallium, cadmium, lead, gold, silver, copper, and aluminium by means of careful density measurements which showed progressive volume changes in the region of and through the melting points. The results of previous experiments are confirmed and amplified.

A. M. Portevin and P. Chevenard⁶³ apply dilatometric methods to the study of the transformations and mechanism of heat treatment of the light alloys of aluminium, magnesium, and silicon and, in general, of alloys containing two-phase, univariant transformations.

S. Beckinsale⁶⁴ reports further results of his investigation into season cracking and its prevention, and deals with the removal of internal stress in 60 : 40 brass. The influence of mechanical methods on the removal of internal stress and the investigation of low-temperature annealing were recorded. Reeling reduces tension stresses in the outer layers of rods or tubes by the production of permanent deformation in tension, with consequent increase in hardness of the layers affected. Malleting, hammering, and springing are uncertain and comparatively ineffective in their results. Low-temperature annealing at 175°–200° C. is superior to other methods, except that reeling of rods or tubes has advantages when it is necessary to straighten these as well as to reduce the amount of stress in them while maintaining the maximum degree of hardness.

N. B. Pilling and R. E. Bedworth⁶⁵ give the results of numerous experiments on the oxidation of metals at high temperatures.

During the course of a research into the cause of red stains in sheet brass, E. A. Bolton⁶⁶ found that most of the staining observed in practice is produced by the interaction of copper oxides in the scale with the pickling acid. The red stains may be removed by means of a strongly oxidising pickle, such as bichromate solutions. The main cause of red stains observed in the works is the impinging of flames upon the metal during annealing.

G. Tammann and K. Dahl⁶⁷ state that intermetallic compounds are brittle owing to their possessing a smaller number of gliding

⁶² *J. Inst. Metals*, 1923, **30**, 121; *J.*, 1923, 983A.

⁶³ *Ibid.*, 1923, **30**, 329; cf. *J.*, 1923, 228A.

⁶⁴ *Ibid.*, 1923, **29**, 285; *J.*, 1923, 357A.

⁶⁵ *Ibid.*, 1923, **29**, 529; *J.*, 1923, 359A.

⁶⁶ *Ibid.*, 1923, **30**, 35; *J.*, 1923, 981A.

⁶⁷ *Z. anorg. Chem.*, 1923, **126**, 104; *J.*, 1923, 361A.

planes than pure metals or solid solutions ; in some compounds no gliding planes were indicated on investigation at different temperatures after shock and subjection to high pressures. All the compounds investigated appeared to become plastic at temperatures approaching their melting points.

F. C. Lea, V. A. Collins, and E. A. F. Reeve,⁶⁸ in a paper entitled "The modulus of direct elasticity of cold drawn metals as a function of annealing temperature," state that for brass tubes the modulus of elasticity, and also the conductivity, have maximum values after annealing at temperatures approximating to 470° C.

Under the heading "Metals for electrical lines,"⁶⁹ a summary is given of the reports of the tests on various classes of wire and cables for overhead transmission lines carried out at the National Physical Laboratory by the British Electrical and Allied Industries Research Association. An account is given of mechanical tests on hard drawn copper, aluminium, and galvanised steel wire in the form of single wires and cables, and of steel-cored aluminium cable.

CORROSION OF NON-FERROUS METALS.

In a general discussion of alloys resistant to corrosion⁷⁰ much interesting information was brought forward. W. H. Hatfield⁷¹ presents the results of a series of experiments on the corrosion of different classes of iron and steel and a number of non-ferrous alloys by waters, various acids, and solutions of salts. For the non-ferrous metals he finds that as regards aluminium the results show that duralumin is distinctly inferior to commercially pure aluminium in its resistance to the various acids and corroding media. As regards the bronzes, aluminium bronze appears to give the best general response, though its yield point in tons per sq. in. is disproportionately low when compared with its maximum stress in tons per sq. in. and with the values obtained from other bronzes.

J. H. G. Monypenny⁷² gives a detailed account of the resistance to corrosion of stainless steel and iron. His contribution includes valuable information concerning the general constitution of stainless steel, the effect of heat treatment, and the influence of variations in composition.

J. Arnott⁷³ discusses the resistance of Monel metal to atmospheric corrosion, sea water, steam, acids, and solutions of alkalis and salts. It was found that at room temperature solutions of

⁶⁸ *J. Inst. Metals*, 1923, **29**, 217; *J.*, 1923, 301A.

⁶⁹ *Metal Industry*, 1923, 411.

⁷⁰ *Trans. Faraday Soc.*, 1923, **19**, 156.

⁷¹ *Ibid.*, 159; *J.*, 1923, 1075A.

⁷² *Ibid.*, 169; cf. *J.*, 1923, 457A.

⁷³ *Ibid.*, 196; *J.*, 1923, 459A.

sulphurous acid attacked the alloy most severely. He concludes that Monel metal is suitable for parts which have to resist sea water, impure water, steam, certain dilute acid solutions, and alkaline solutions of all kinds. U. R. Evans⁷⁴ discusses at length the mechanism of the so-called "dry corrosion" of metals, and draws the following conclusions:—Experiments on the behaviour of apparently dry metals, roughened with emery, show that no corrosion occurs when they are kept over sulphuric acid, and only slow, superficial corrosion when they are kept over water. The rate of attack is greatly increased by the presence of volatile electrolytes in the air, sulphur dioxide being most dangerous to iron and nickel, ammonia to copper and its alloys, and hydrogen chloride to zinc and aluminium. Corrosion of metals by volatile electrolytes appears to require some moisture, but proceeds in air which is distinctly unsaturated. Special phenomena occur at the contact of dissimilar metals, apparent electro-chemical protection being observed in some cases. The phenomena are best explained if it is considered that electro-chemical action occurs in the adherent (usually invisible) film of moisture. Volatile electrolytes increase the conductivity of the film and thus accelerate corrosion. Where they tend to produce hygroscopic corrosion products, they bring about the absorption of further moisture, and thus increase the thickness of the film.

Other contributions are by J. F. Kayser on "Heat and acid resisting alloys (Ni-Cr-Fe)",⁷⁵ and by F. Orme, "Corrosion tests on certain nickel alloys."⁷⁶

U. R. Evans⁷⁷ believes that at ordinary temperatures the phenomena of corrosion as at present known are electro-chemical in character. He distinguishes two types of corrosion, one characteristic of the more reactive metals in which hydrogen is evolved, the other depending upon the diffusion of oxygen to the metallic surface.

⁷⁴ *Trans. Faraday Soc.*, 1922, **18**, 201; cf. *J.*, 1923, 458A.

⁷⁵ *Ibid.*, 184; *J.*, 1923, 1074A.

⁷⁶ *Ibid.*, 199; *J.*, 1923, 1075A.

⁷⁷ *J. Inst. Metals*, 1923, **30**, 239; *J.*, 1923, 981A.

ELECTRO-CHEMICAL AND ELECTRO-METALLURGICAL INDUSTRIES.

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ELectRIC FURNACES.

RECENT progress in the application of electric furnaces is again mostly apparent with types of a moderately low temperature range, and is characterised by the more extended use which is being made of electric furnaces in the manufacture of castings, in steel-smelting furnaces, and in furnaces for the annealing and heat-treatment of non-ferrous metals. The development which has recently taken place in this last connexion has been particularly marked in the United States. The main advantages found by this procedure are due to the adaptability of the furnaces, the uniformity of heating obtained, and the completeness of control which can be gained of temperature and atmosphere, and the manipulation. The continuous electric furnace, which has recently received more extended application, enables articles which enter cold at one end to be removed at the required temperature at the outlet. Iron castings can thus be heated continuously in an identical manner. On the ground of cost of heat, the electric annealing furnace has difficulty in competing with the fuel-heated type, but the advantage obtained is in the more certain realisation of the conditions desired.

For the melting of metals and non-ferrous alloys, such as copper, bronze, brass, aluminium, zinc, cupro-nickel, and similar alloys, electric furnaces are continually receiving increasing application and the developments in this branch have probably been more marked than in any other. The principal types of furnaces for the above object may be classified as the open arc, the muffle type,¹ the resistance type, and the induction furnace. The types most commonly used in the first category are stated¹ to be the Snyder, Booth-Hall, Volta, and Giolitti furnaces, the last one being particularly used in brass and bronze foundries. Of muffle furnaces, the only representative is that of the General Electric Co. The most popular resistance furnace is that of Baily, and among induction furnaces, the Ajax-Wyatt and General Electric Co. types are found very satisfactory.

¹ *Le Four Elec.*, 1923, 32, 160.

In a review of recent developments in electric furnace practice by E. T. Moore,² it is pointed out that in the application of electric furnaces for the production of various forms of steel a rapid recovery has now taken place from the reaction and slump which followed the great extension of installations during the war period. A marked tendency has been shown to the use of a greater number of smaller furnaces. In the production of malleable and grey iron castings, the main advantage of electric furnace treatment is that any degree of superheating may be obtained and iron much lower in phosphorus content may be used than is necessary in order to produce fluidity with ordinary means of production. The application of electric furnaces in this particular connexion has, however, been very slow. In a recent type of Héroult furnace, the reactance due to the large currents employed has been diminished by using conductors of copper pipes which also serve to carry water to the electrode holders and the electrode coolers. In this way, about one-third as much copper is required as when using bars, and the conductors can be brought close together, thus reducing reactance and making it possible to have longer leads and at the same time have them extend beneath the floor. A further advantage is gained by this method where it is necessary to carry the bus-bars over a hot furnace. The mast or structure which was formerly erected over the furnace to support the electrode arms and holders necessitated carrying the conductors over the top of the masts in order to avoid proximity to the iron parts and involved overhead flexible cables. In the new designs the mast is eliminated and the electrode arms and holders are supported from below. A description is given of the modifications which have been made in the arrangement of the electrode arms which enables the electrodes to be brought as close as possible to each other and to the centre of the furnace.

The transformer reactor and high-tension equipment are placed beneath the floor, which makes it more convenient to have the electrode-supporting mechanism attached to the furnace either at the bath, opposite the teeming spout, or on one side. Additional external reactance is applied to lower the power factor to 90%. Improvements are also described which have been made in the Greaves-Etchells furnace and the Moore "Lectromelt" furnace. An improvement has been effected in the durability of carbon electrodes by securing an increase in density or diminution in porosity.

In describing the development of the large electric melting furnace, F. Hodson³ points out that a limitation is imposed on the

² *Blast Furnace and Steel Plant*, 1923, 11, 153.

³ *Amer. Inst. Elec. Eng. J.*, 1923, 42, 600; *Iron Trade Rev.*, 1923, 72, 1462; *Foundry*, 1923, 51, 561.

size of furnaces with three top electrodes in that this type does not lend itself to multiples of three electrodes. On account of the current-carrying capacity of the largest electrodes which are available commercially, a limit has thus been reached with furnaces of a capacity of 40 tons of metal.

A furnace which has been designed by Greaves and Etchells consists of an arc-resistance type which, on normal operation, introduces two phases of the three-phase power supply line through two or more top electrodes and the third phase through the whole of the furnace hearth. By the use of four or more electrodes, the system and design which are described enable the whole of the power to be put through top electrodes or, by change of the position of an oil switch, through top electrodes and the furnace hearth, a balanced load being obtained by either method. Considerable flexibility of operation is possible as the top electrode and high voltage can be used when melting down or when starting up a cold furnace, and the top and bottom electrodes when the molten bath is obtained and for refining and superheating after melting the metal. The principle employed consists in connecting the two top electrodes or groups of electrodes to two arms of the secondary of a star-connected transformer, while the base of the hearth is connected to the third arm wound to give a lower voltage, and the primary windings of the transformer are in delta. Units of this furnace of 60-80 tons capacity are under construction for the Ford Motor Co., Detroit, U.S.A.

It is pointed out that the Söderberg continuous electrode, now operating in a number of electric steel furnaces, may also have considerable bearing on the future design of large electric furnaces.

In an article by F. V. Andreac⁴ some problems in electric furnace operation are considered. Based upon the theory that the reactance of a three-phase electric furnace does not depend upon the load but is a constant, depending on the arrangement of the conductors, the general equations of the three-phase furnace are developed and discussed. The transformer action which takes place in the bus-bars between the different phases is considered. When only voltage, current, and total power are concerned very simple expressions can be used which are entirely satisfactory in practice. A few methods are suggested to reduce the unbalancing of the load. The conditions obtaining in two-phase operation are defined. In this case the load must be considered as connected in star, the bottom of the furnace being the neutral. The electric energy is in this case transformed into heat in three separate zones situated under the three electrodes. It appears probable that the load resistance is furnished by an arc in an atmosphere of vapours under pressure. Measurements are made with currents

⁴ Amer. Inst. Elec. Eng. J., 1923, 42, 498.

varying from 6000 to 24,000 amps. per phase. The reactance per phase measured on the low-tension side is found to be practically constant over the whole range of loads. The reactance depends upon the disposition of the bus-bars and other conductors carrying the current into the furnace. The load circuit, or the part of the circuit where the electric energy is transformed into heat, does not show any reactance and acts like a pure resistance.

The points which it is necessary to consider in the design of an electric furnace are outlined by L. P. Barton.⁵ The main types of transformers now in use are the Héroult, operated at a voltage of about 110 volts, and the Pittsburgh or "Lectromelt," with a voltage of nearly twice this amount. It is imperative to make the furnace leads as short as possible, as the closer the transformer is to the furnace the better will be the power factor. The electrical connexions or methods of transformer wiring show wide variations on the different furnaces and consist of the two-, three-, or four-phase system. The majority are operated with three-phase connexions, due to the fact that nearly all power supply is of this form. The use of bottom electrodes is generally being eliminated in modern furnace design. Opinion is at present equally divided as to the superiority of graphite or carbon electrodes. Operating costs per ton of metal are practically the same for both.

The use of automatic current regulators gives an advantage in the power consumed per ton of metal and in the longer life of the refractories and electrodes. With regard to metallurgical features the nature of the hearth is the most important consideration. A rather deep hearth is found to favour rapid operation and is recommended for acid working, while a shallow hearth offers the best conditions with a basic slag. The thickness of the furnace walls will depend on the size of the furnace. In the great majority of cases, in both acid and basic operation, silica-brick walls are used. Amongst other special refractories there has been introduced a fused magnesite which does not shrink and offers marked possibilities for the electric furnace. The roof is generally of silica brick though carborundum is used. Reference is also made to the subjects of doors, arrangement of electrodes, shape of furnace, tilting devices, electrode holders, cooling rings and economisers, general cooling arrangements and charging devices.

A critical review of different types of electric furnaces is given by M. Fourment.⁶ It is concluded that for the melting of alloys, resistance furnaces, of which the main representative is the Baily type, have the great advantage of robustness and simplicity; they are adapted for all types of current supply and are easily main-

⁵ *Blast Furnace and Steel Plant*, 1923, 11, 272.

⁶ *Bull. Soc. Ing. Civ. France*, 1923, 76, 446.

tained. The consumption of refractory lining is lower than in other types; the resistances deteriorate only slowly and are readily replaced; the metal is heated progressively and there is no possibility of burning. There is no consumption of electrodes and water-cooling is avoided. The disadvantages of the type are the impossibility of attaining high temperatures, and the higher current consumption compared with other types.

With induction furnaces, heat is generated in the interior of the bath, thereby insuring a high thermal efficiency and a lower power expenditure than in any other type. Other advantages are:—Absence of electrodes, rapidity of fusion, low losses through volatilisation, the possibility of employing a large range of voltages for the primary, and the ready production of a large range of temperatures by adjusting the intensity of the current through the primary. On the other hand, induction furnaces are not readily suited for refining and require, except in the case of the high-frequency type, a preliminary charge of molten metal; moreover, on account of the low resistance, the power factor or value of $\cos \psi$ is low.

Arc furnaces provide the most flexible type. With medium capacities, the current consumption is intermediate between that of resistance and induction furnaces, while with large units it is equal to the latter. The disadvantages possessed are the necessity which is entailed of renewing the electrodes, the use of water-cooling, and the disturbances which are set up in the supply circuit, especially with large units, though this effect may be diminished by automatic regulation of the electrodes. The losses due to oxidation and volatilisation are considerable.

The electrical efficiency is affected appreciably by losses due to contact of the electrodes with the collars or glands where they pass into the furnace enclosure and to the resistance of the portions of the electrodes exterior to the furnace. Rotating and oscillating furnaces are only suited for use with monophase current through possessing only two electrodes, and current from a three-phase circuit can only be employed by loss of efficiency.

A new type of induction furnace is described which has been constructed by the Compagnie Française des Métaux. This is designed for the melting of non-ferrous metals and preparation of alloys, and is arranged to work continuously or with varying temperatures and to permit readily the decanting of molten metal from the residual slag. The furnace is constructed for use directly on a three-phase supply of 220 volts at 50 cycles, and is provided with three magnetic cores and a triangular channel of a rectangular section similarly to the Röchling-Rodenhauser type. The rotating magnetic field leads to circulation of the metal. As a refractory for this furnace a material known as "corindite" is

used, consisting of a mixture of sillimanite, $\text{Al}_2\text{O}_3\text{SiO}_2$, and corundum, Al_2O_3 , which is applied in a fused condition, the melting point being 1900°C ., and its durability being considerably higher than that of magnesia bricks. Units of this furnace of 100—200 kw. capacity are in operation at Castelsarrasin in France. A unit of 100 kw. contains 600 kg. of metal and melts brass with a power consumption of 250–300 kw.-hr. per ton of metal.

An historical *résumé* is given by E. W. Lewis⁷ of the commercial applications of the electric furnace. Its early development was focussed on the search for an economical means of producing metallic aluminium. A summary is given of the different types of furnaces now in use. The development of induction furnaces has not kept pace with metallurgical operations and, at the present time, the arc type easily outnumbers induction furnaces in industrial applications, particularly in the metallurgy of steel, ferrous and non-ferrous metals and alloys. The outstanding difficulty experienced with induction furnaces has been to find a suitable lining material to withstand the heat, and the demand for the use of an exceedingly low frequency power. The majority of arc furnaces, which are used in capacities of from 1 ton to 40 tons, are built on the Héroult principle. In several types of modern furnaces, application is made of the combined principles of the arc and resistance. For the melting of steel castings, the power expenditure varies from 500 to 600 kw.-hr. per ton, and for refined steel from 700 to 1200 kw.-hr. per ton. For the heat treatment of metals, the furnaces used are of the resistance type. For the melting of iron ores, the type of furnace which has been found most serviceable is the Elektrometall furnace. In modern practice, firebricks are replacing magnesite as a furnace lining. Apart from its application in the manufacture of steel, the electric furnace has proved highly successful in the manufacture of alloy ingots, such as ferro-silicon, ferro-tungsten, ferro-titanium, and ferro-chromium. Three-phase furnaces have been found to be most economical for the ferro-alloys of silicon, manganese, and chromium, which have lower melting points, and single-phase for those of molybdenum, vanadium, uranium, and titanium.

A recent marked development in electric furnace practice is in the automobile industry where it is tending to become common practice even at a slightly higher cost. The advantages gained in this case are due to the ease of control and the regularity and uniformity of the results obtained. One of the Ford factories in America contains an electric furnace forming a connected load of 14,000 kw. for the heat treatment of motor bearings. The carbon resistance type has been widely installed and provided with automatic control of temperature. The heating is effected by carbon

⁷ *Engineering*, 1923, 116, 257.

rods immersed in a trough of sand, the load being controlled by variation of the secondary voltage with tappings from a special type of transformer.

A highly efficient type of furnace was developed during the war for the heat treatment of gun barrels, and has since been adapted to the motor industry. The heating unit comprises a ribbon of chrome-nickel alloy, which is supported by a cast-iron plate with an insulation of refractory material. The units used are of 400 kw. and take three-phase current at 440 volts. The temperature is controlled by an automatic cut-off arrangement.

In the annealing of glass, the electric furnace is rapidly supplanting the fuel-fired furnace, due to the accurate control of temperature, uniformity of the heat application, and the even distribution of heat.

An illustrated description is given by E. Zeulmann⁸ of a number of applications of electric heating, both for domestic and workshop purposes. These include water boilers, radiators of various types, and appliances for heating raw material in process of manufacture.

The application of the electric furnace to vitreous enamelling is described by J. L. M. Yardley.⁹ A description is given of the technique and economics of the operation and the advantages gained by electrical heating.

An account is given by E. W. Roeser¹⁰ of an electrical oven, which has been installed for the baking of vitreous enamel as applied to iron and steel plates. The furnace consists of a lower and upper rectangular chamber, the side walls of each carrying refractory supporting bricks upon which nichrome ribbon is suspended and arranged in a recess in the side walls so as to avoid contact with the incoming work. The windings are distributed in the side walls of both upper and lower chambers and in the front walls of the lower chamber in such a manner as to compensate for the extra heat loss from the charging doors and to cause a uniform distribution of heat throughout the working space. Additional nichrome wire is welded to the terminal strips of the windings, which then pass through a wall bushing and are secured in place by a set screw in a collar washer. The products to be enamelled, are, during heating, supported on a projecting refractory ledge which separates the lower and upper chambers. In order to diminish heat losses, air-cell insulating brick, 12 in. thick, is used to surround the heating chamber and is reinforced by an outside wall made up of a layer of red brick. The windings are connected in delta and supplied with current at 230 volts, 3-phase, 60-cycle. A Leeds-Northrup automatic temperature control device is

⁸ Z. Ver. deut. Ing., 1923, 67, 617.

⁹ Chem. and Met. Eng., 1923, 29, 55; Elec. World, 1923, 82, 327.

¹⁰ Foundry, 1923, 51, 632.

employed. The e.m.f. from a thermo-couple mounted in the furnace causes an unbalanced condition in the galvanometer system proportional to the temperature, and by means of a relay, controls are actuated which raise or lower the voltage applied to the furnace. At the temperatures employed, varying from 650° to 870° C. according to the class of work, the temperature can be controlled to within 3°. The power consumption, when employing a temperature of 870°, is 1 kw.-hr. for each 6-7 lb. of metal. The capacities of the furnaces now in operation range from 60 to 95 kw.

A general discussion is given by F. W. Brooke¹¹ of the design of various electric furnaces, such as the special box type, the car type, the recuperative and continuous furnaces, and their advantages and disadvantages are referred to. In the car type, conveyors with the substances to be heated pass through the furnaces. The continuous systems described are of the "push," "gravity roll," and "walking beam" types. Attention is drawn to the method of handling materials for these furnaces so that a uniform temperature may be maintained.

Laboratory and Small Furnaces.

The different types of electric furnaces which have been developed are reviewed by C. R. Darling,¹² who gives an outline of the economics and general advantages attending their use in comparison with fuel-heated processes. The types of furnaces which are described include the wire-wound furnace which was devised by Heraeus in 1902, the later type in which the platinum originally used is substituted by nickel-chromium alloys, and the various forms of muffle furnaces of which units with tubes 5 ft. long and 1 ft. diameter are now in common use. In a usual pattern containing tubes 1 ft. long and 2 in. diam., the power required to maintain a temperature of 1000° C. is 0.5 kw. for a single-tube furnace, and 1.2 kw. for one in which four tubes are worked simultaneously. In the laboratory this type of furnace is used for experimental work on the heat-treatment of metals, for incinerations and chemical combustions, standardising pyrometers, and as a substitute for gas-heating for many other purposes. In the workshop, they are found of great service in hardening and tempering miscellaneous carbon-steel articles. A double muffle furnace designed by the Leeds Construction Company consumes 5 kw., is of a rotational type, and is employed for the continuous heating of rivets. The Wild-Barfield furnace is employed for the hardening of steel and has a capacity up to 100 lb. of steel per hour; it is provided with an automatic temperature control by means

¹¹ *Trans. Amer. Electrochem. Soc.*, 1923, **33**, 149.

¹² *J. Roy. Soc. Arts*, 1923, **71**, 324.

of a loop of silver wire, through which the current passes and melts when a temperature of 961° C. is reached, thus breaking the circuit.

For higher temperatures such as 1800° C. which are needed in the annealing of tungsten, furnaces wound with tungsten and molybdenum have been applied and heating is conducted in an atmosphere of hydrogen. For still higher temperatures, such as 2000°–2500° C., which are employed in the standardising of optical pyrometers, various types of carbon tube furnaces which have been applied are described, including the type utilising the contact resistance between a number of separate graphite or carbon rings, that using a carbon strip in the form of a spiral cut from a graphite tube, and the various forms of granular carbon resistance furnaces. A later form of furnace due to Hancock consists of a number of carbon rods in series, running along the outside of the refractory chamber, and forming a kind of cage around it. The ends of the separate rods are connected by graphite strips, and both are preserved from oxidation by covering with a carbon composition, highly compressing and baking at a high temperature.

In describing appliances used in conjunction with resistance furnaces, reference is made to automatic cut-outs and temperature indicators which are actuated by the magnetic properties of the steel under treatment, by utilising the effect of demagnetisation occurring at a definite temperature. Types described are the Bastian, the Wild-Barfield, and the Stopford-Darling.

An internally wound electric furnace is described by H. Forestier,¹³ and is made up as follows:—About 4 m. of nichrome wire is wound on a metal tube 3–4 cm. diameter, and the coil is covered with a layer of alundum cement, 1–2 mm. thick. This is dried, the tube is placed in the axis of an asbestos mould about 10–12 cm. diam., and the annular space filled with quick-setting cement. The whole is then surrounded with a layer of about 3–4 cm. of asbestos wool, the metal tube is withdrawn, and the furnace is ready for use. The furnace described may be heated to 1000° C. in 30 mins., and cools to 100° C. in 1½ hr. The power consumption under these conditions is about 0·5 kw., or 4·5 amp. at 110 volts.

Theoretical.

In a discussion of the theory of high-frequency induction furnaces by G. Ribaud,¹⁴ consideration is given to the relation between frequency of current, resistance of the bath, and the nature of the charge. It is concluded that the energy expended in the body is proportional to the square of the effective intensity, to the diameter

¹³ *Bull. Soc. Chim.*, 1923, 33, 999; *J.*, 1923, 894A.

¹⁴ *J. de Physique et de Radium*, 1923, 4, 185.

of the charge in the furnace, and to the square roots of the specific resistance and of the frequency. The state of division of the substance is important, and for each substance there is an optimum degree of fineness. For bodies of low conductivity the output of the furnace passes through a maximum for a specific resistance depending on the frequency.

An investigation of the progressive changes which are observed with various types of arcs formed with increasing currents is published by P. A. Bassett.¹⁵ Carbon arcs and ordinary flame arcs are found to change their behaviour fundamentally with large currents. The tendency to produce two arc flames, a positive and a negative, is present in an obscure form in practically all arcs. In the high-intensity arc this phenomenon has been enhanced to a point where the two flames are separate and distinct, and each flame performs a separate function. The effect is caused by the repulsion of the main arc from the end of the negative pole. The high intrinsic brilliancy obtainable with this type of arc and its application to searchlights are discussed. In the case of cored electrodes, an investigation is made of the zone in which carbides are formed and the part played by them in the brilliancy produced.

The relation between current, voltage, and the length of carbon arcs is discussed by A. H. R. Westman.¹⁶ Formulae connecting current, voltage, and arc length, which have been derived previously by Mrs. Ayrton and by Steinmetz, were based on measurements of current amounting to about 30 amps. The present work gives the results of measurements made with currents up to 770 amps. The conditions have been found under which a steady arc can be maintained between carbon electrodes with currents of 300 to 400 amps., and a fairly steady arc with currents up to 800 amps. Humming, swinging, and groaning arcs have been described, with a way to avoid hem. It is found that an arc can be maintained easily with a potential as low as 20 volts. For currents between 300 and 400 amps., and potential differences across the arc of 55 to 20 volts, the potential in volts is approximately equal to the distance between the electrodes in mm., while for currents of 700 amps. or so, the voltage is less than the distance. The formulae proposed by Mrs. Ayrton and by Steinmetz for low currents are found to be not in agreement with the experimental results for high currents.

In a continuation of this investigation by A. E. R. Westman and W. J. Clapson,¹⁷ measurements were made with currents from 120 amps. to 700 amps. and voltages from 15 to 60, and a technique is developed for determining more accurately the relation between

¹⁵ *Trans. Amer. Electrochem. Soc.*, 1923, 319 (*Advance Copy*).

¹⁶ *Ibid.*, 1923, 43, 171.

¹⁷ *Ibid.*, 1923, 87 (*Advance Copy*).

current, voltage, and the length of carbon arcs. These results lead to the conclusion that $e = 0.99L$, where e is the voltage across the arc, and L the length in mm. from the tip of the cathode to the bottom of the anode crater.

Calculations on current conductors in electric furnaces are made by A. Pasquier.¹⁸ An estimate is made of the distribution of heat along the carbon electrodes by taking into account the Joule heat developed by the passage of the current, the conduction from the heated furnace and the radiation losses. Formulae are derived which permit the calculation of the optimum length, breadth, and shape of electrodes for given current and furnace temperature.

ELECTRODES AND REFRactories.

Data are given by F. Gall¹⁹ relating to the conductivity and other properties of carbon and graphite, followed by a general account of the processes of manufacture of electrodes.

Information is given by R. C. Gosrow²⁰ on the selection of materials for the refractory linings of electric furnaces, and on the methods to be employed in the setting of bricks. A classification is made of the refractory materials, according to whether these are acid, neutral, or basic, and the form in which these can be obtained, whether as brick or powder. Formulae for the refractory surface coating of walls are given. The selection of materials for roof construction is considered.

CALCIUM CARBIDE MANUFACTURE.

In an account which has been published of the developments of the calcium carbide industry²¹ a description is given of the nature of the chemical reactions which take place and the effect of different impurities. With reference to the electrical features, the large Continental and American furnaces are of the double three-phase alternating current type and have a rated capacity up to 10,000 h.p., the energy consumption being 1 h.p.-yr. per ton of carbide produced. Modern furnaces are mostly of the tapping variety, the carbide being allowed to run from the furnace in the molten state. These furnaces may be divided into two types, those with two or more electrodes admitted through the roof and those with one electrode or more through the roof and one electrode at the base. The former type involves the higher electrode consumption but the latter type involves structural difficulties and has other disadvantages. The introduction of polyphase current for the operation of electric

¹⁸ *Rev. Mét.*, 1923, **20**, 591.

¹⁹ *Bull. Soc. Ing. Civ. France*, 1923, **76**, 468.

²⁰ *Chem. and Met. Eng.*, 1923, **29**, 1181.

²¹ *Elec. Rev. (London)*, 1923, **92**, 126.

furnaces has effected a marked improvement in efficiency as well as an increase in capacity. In some of the modern American furnaces, triple three-phase systems are now employed with nine electrodes, the total power consumption being about 15,000 h.p., and the output 160 tons of calcium carbide in 24 hours. These furnaces are covered in, so that the carbon monoxide evolved can be collected and utilised and the thermal losses are considerably lessened. Consequent on the introduction of massive transformers, there is now a tendency to build furnaces of a much larger capacity. The introduction of multi-phase current has also given much assistance in the distribution of the load in generating stations.

IRON AND STEEL PRODUCTION.

Electrothermic Smelting of Iron Ores.

Data are given by C. de Coussergues²² on the number of electric furnaces in operation in different countries—of which Sweden occupies the first place—for the production of pig-iron. The furnaces employed are all of the vertical shaft or blast-furnace type, and, in nearly all cases, use wood charcoal as the reducing agent for the iron ore. Under normal conditions the electric smelting furnace can only compete with the blast furnace for pig-iron production in countries where water power is very cheap or where coke^{*} is very dear. Under special conditions, however, electric furnaces may be employed for the production of special forms of pig-iron. In France, for instance, ferro-silicon and pig-iron are being prepared in this manner for the production of malleable castings, and in America there is an installation of an electric cupola furnace operated in conjunction with an electric refining furnace.

An account is given by L. Lycke²³ of experiments which have been carried out over a period of 4½ months on a new type of electric pig-iron furnace with two shafts. The production of cast-iron in such a furnace demands that the three following conditions be fulfilled: high temperature, excess of fuel, and long working period. In general the simultaneous attainment of these three conditions is not easy, so that the successful production of cast iron in the electric furnace is difficult. Results are given comparing the type of furnace used with other types of electric furnaces, and the heat balance of the furnace over a working period is discussed.

An account is given by C. E. Williams, C. E. Sims, and C. A. Newhall²⁴ of an electric furnace process for detinning and the production of synthetic grey iron from tin-plate scrap. Experiments were conducted in a small electric furnace in which tin-plate

²² *Bull. Soc. Ing. Civ. France*, 1923, **76**, 543.

²³ *Stahl u. Eisen*, 1923, **43**, 110; *J.*, 1923, 456A.

²⁴ *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 192; *J.*, 1923, 503A.

scrap was melted with various addition agents in attempts to remove the tin from the iron. Sodium chloride, iron sulphide, and an oxidising slag were used under various conditions. It is impossible to remove most of the tin in tin-plate scrap or similar material by any of the electric furnace melting processes tried; moreover it is impracticable to attempt any detinning by these means. No tin is volatilised ordinarily when cast iron containing it is melted in the electric furnace. The amount of tin volatilised during melting in the cupola may be as much as 50% in some cases, whereas in others it may be practically *nil*, depending upon the amount of surface of metallic tin exposed, and the oxidising condition of the blast. Lead can be removed completely from iron coated with lead and, likewise, zinc can be largely removed from galvanised scrap by melting in the electric furnace. A tin content of 1% or less does not seriously affect the physical properties of cast iron. It is recommended that tin-plate scrap and used tin cans, which cannot profitably be treated by any of the established detinning processes, may be treated in the electric furnace to produce synthetic cast-iron, using low-grade, tin-free scrap for dilution to reduce the tin content of the product to within safe limits.

Electric Steel Furnaces.

A review of the recent progress made in the manufacture of steel in the electric furnace is given by C. de Coussergues.²⁵ The different systems employed are described and a discussion given of the factors which determine the output for a given power expenditure and of the direction in which improvements are to be looked for in future designs of furnaces. The three classes of furnaces now in use are: (1) the resistance type in the form of induction furnaces, (2) the open arc type, and (3) the arc-on-metal type. The induction type possesses certain advantages for special classes of work but for the high temperatures required in the treatment of iron a sufficiently robust type for large output does not appear to have been developed. Open arc furnaces have developed in the direction of small installations. The majority of furnaces in use for steel production are of the arc-on-metal type. With induction furnaces, the disadvantages which are most apparent with small units are low efficiency through heat losses and the "pinch" effect which prevents the attainment of a high temperature. With large units, on the other hand, the serious reactance involves the use of very low periodicities in order to obtain a reasonable power factor. A periodicity as low as 5 is, for instance, necessary with a furnace of 8 to 10 tons capacity. A further disadvantage is that the slag is not heated except by contact with the metal and is thus less

²⁵ Bull. Soc. Ing. Civ. France, 1923, 76, 423.

reactive. Induction furnaces are only really practicable for hard and special steels and have only developed to any extent in Norway and Germany. In the open arc type, the arc is formed between two or three electrodes above and in close proximity to the surface of the bath. With small units a voltage as high as 150 may be used. The main disadvantages are the fact that the heat is not produced in contact with the bath and a large proportion is radiated on to the walls and roof of the furnace.

In the arc-on-metal type, an arc is maintained between the electrode and the surface of the bath. This system is the one most generally in use with steel furnaces and is employed with single-, two-, or three-phase current. In nearly all cases the use of multiple electrodes is preferred. With two-phase furnaces, two suspended electrodes are generally employed, while the common return is in some types connected to the metal of the bath and in others to a conducting hearth under the bath. By means of Scott connexions, current is taken from a three-phase supply.

In order to employ the highest practicable voltage, the length of the arc must be extended as far as possible, but, at the same time, this must remain wholly within the slag or excessive radiation of heat to the roof occurs. In the present practice, a voltage of between 45 and 55 between the end of each electrode and the surface of the bath is employed and the roof is raised one metre above the level of the bath. With small furnaces the roof is somewhat lower and the electrode voltage lower by 5 to 10 volts. In the latest installations in France and America use is made of a system of variable voltage whereby a potential of 120 volts is employed during the fusion and later lowered to 80 volts, while for the final stages this is further reduced to 50–60 volts.

The chief representative of the three-phase type of furnace is that of Héroult. The main directions in which improvements have been made in the original type are, apart from the size, in the shape and structure of the bath and in the reduced clearance and improved arrangement in the passage of the electrodes through the roof of the bath, thus ensuring better sealing, and in the higher voltages applied. The power consumption for a given output of steel varies largely with the nature of the charge and the type of steel to be produced. For a 1% carbon steel from mill turnings, 389 kw.-hr. per ton may be taken as an average value, while for an extra soft steel from 90% turnings, 1067 kw.-hr., measured at the furnace terminals, may be allowed for. The two main factors which limit the efficiency of furnaces consist of heat and electrical losses. The heat loss involves the consideration of insulating materials. With the electrical loss, the reactance is not serious as a power factor of 90% is often obtained. The most serious loss arises from bad contacts or by the inductance of metallic masses

close to the circuit. This effect is accentuated by the low voltage at which the current is employed.

An historical account of the development of the Héroult furnace and its distribution throughout the world is given by J. Suhr.²⁶ The conditions affecting the development of electric steel manufacture in France are described. In comparing the conditions in France with those in America, the view is put forward that the reason why the electric furnace has not been as generally adopted for steel manufacture in France as in America is largely due to the fact that French metallurgical workers possess so much experience and skill that they can produce, by the ordinary processes of manufacture, steel quite equal in quality to electric steel. In America, owing to lack of proper training, the steel workers can only produce steel of this quality by exceptional means, such as electrical heating.

In future applications of the electric furnace in steel manufacture, it is considered that the highest economy and efficiency will be obtained by utilising it solely for the refining and finishing operation in association with the basic process. Units of 30 to 35 tons consuming 2500 to 3000 kw. are preferable on account of their adaptability. The quality of steel is discussed and notes are given on practical points bearing on the processes of desulphurisation, dephosphorisation, and deoxidation. Data are given on power consumption required for different types of steel, together with dimensions and electrode current density.

A series of tests has been conducted with a standard 6-ton counterweight type of Héroult furnace at the Halcomb Steel Co.²⁷ The tests were designed to obtain accurate data on the heat losses in furnaces, operating data on electrodes, the merits of dual voltages, the effect of high voltages for melting purposes, and electric furnace phenomena. The furnace used was supplied by three 500 kv.-a. transformers arranged with star connexions on the high-tension side to give 70 volts on the secondary. The inherent reactance was 5% and, in addition, three 25- kv.-a. external 3% reactors were used on the incoming lines, with switching arrangements for cutting them in or out as desired. The maximum unbalancing of phase found on an individual furnace amounted to 340 kw. or 21% of the connected load. During the melting period the greatest value of current obtained was 1.1 times normal. With the electrodes submerged in the bath the greatest short-circuit current was 3.66 times normal. High-frequency waves of the order of 5000 cycles are set up by the arcs in the furnaces as shown by oscillograms. External reactance in the furnace line will reduce the power factor and the amplitude of load peaks of swings. During

²⁶ Bull. Soc. Ing. Civ. France, 1933, **76**, 593.

²⁷ E. T. Moore, Elec. World, 1923, **82**, 698.

the melting period the power factor averages 90%, during the refining period it averages 88%, and for the entire heat the average power factor is 89%. Furnace transformers should be built with 5% inherent reactance and variable-tap external reactors are advisable, particularly on 25-cycle circuits.

It is advisable to employ at least 27 in. clearance from the refractories for all the electrodes in this type of furnace and to increase the capacity of the transformers to 2000 kw.; the limits of dimensions for a single unit when melting and employing one set of electrodes and 25-cycle current, is considered to be of 25 tons capacity with a power consumption of 4500 kv.-a. For hot-metal working a 40-ton furnace with 3300 kv.-a. capacity and 24 in. electrodes is very satisfactory. For melting furnaces using one set of electrodes on 60-cycle circuits 15 tons is the maximum size recommended, but 40-ton furnaces may safely be used for hot metal work. With regard to the relative merits of 25 cycles and 60 cycles for furnace work, more reactance must be used on 25 cycles, but more energy may be admitted to the furnace. Arcs on 60 cycles have a greater tendency to persist than arcs on 25 cycles. Short circuits in furnaces do not generally occur across all phases at once. The unbalancing effect will not cause any disturbance to a power system of adequate capacity. Results are given of detailed measurements and chemical analyses during the preparation of alloy steels.

The Chaplet process for the direct production of steel from iron ore is described by the inventor.²⁸ In this furnace, a conducting hearth is used and a vertically-suspended electrode. Experiments at Giffre with a furnace of 150 kw. have shown that molten steel can be obtained in this type of furnace with a facility equal to or even greater than cast iron. The steel produced by this process is said to possess characteristic properties, in that a steel with 0·2% carbon is as soft and malleable as ordinary steel with 0·08% C. By carefully protecting the metal from contact with air a steel has been produced with 2% carbon which could be hammered cold in spite of its hardness.

A further description of the Chaplet furnace is given by W. Mason.²⁹ The current supplying the arc enters by one or more vertical electrodes through apertures in a domed roof and leaves through a base electrode which is embedded in the hearth of the furnace. Slag is first charged into the furnace, then the ore to be reduced mixed with carbon in suitable proportions. The reduction begins under the action of the arc and the reduced metal filters through the slag and collects on the bottom. In experiments with this furnace in which more than 15 tons of metal was produced, the

²⁸ *Bull. Soc. Ing. Civ. France*, 1923, **76**, 606.

²⁹ *Elec. Rev. (London)*, 1923, **93**, 190.

charge was a mixture of haematite ore and dried powdered charcoal. For the production of soft iron, a power consumption of 3430 kw.-hr. was required per ton with a furnace of 120 kw. and 2600 kw.-hr. with a furnace of 200 kw. The consumption of electrodes amounts to 55—57 lb. per ton of soft steel.

An account of the procedure followed in the manufacture of steel from scrap by acid operation is given by J. M. Quinn.³⁰ The controlling factor in the operation of the acid process seems to be the quantity of iron oxide present at the time the charge is melted, whether present with the scrap as rust or whether it results from oxidation due to air leak in the furnace, or from the addition of iron ore. The main difference between acid and basic steel is determined by the free or nascent silicon, which is displaced from silica by carbon at high temperatures and exerts an effective deoxidising action on the steel, increasing its solidity and freedom from blow-holes. Ferro-manganese is not so effective as silicon. Aluminium is the most powerful deoxidiser and is used in special cases, the alumina formed combining with the slag. Other reducing agents used are titanium and calcium.

In an article by Allamel³¹ on the position with electric furnaces in Sweden, it is pointed out that in that country the type of furnace most generally used is the Rennerfelt, in which the arc is magnetically deflected downwards on to the surface of the bath. A movement of the metal away from the arc is avoided, a condition which facilitates the disengagement of gases from the metal.

Induction Furnace.

A description is given by O. von Keil and W. Rohland³² of measurements which have been made with a Röchling-Rodenhauser furnace to enable a complete estimate to be made of the disposal of materials and the heat and electrical input. The furnace employed was of the double-ring type employing two induction cores. Two-phase current was applied from a three-phase circuit by means of Scott connexions, the current consumed in the primary of the furnace amounting to 150–200 amps. at a voltage of 2000 and periodicity of 16·6 cycles. The capacity of the furnace was 8–12 tons of metal. Temperature measurements were made by means of pyrometers and heat conductivity and radiation losses were estimated separately. For this purpose measurements were made of the temperature and volume of air circulating around the furnace. Molten steel was admitted to the furnace and the usual refining treatment applied, including removal of phosphorus and sulphur, addition of alloys, and adjustment of the carbon. The

³⁰ *Iron Age*, 1923, 111, 1177.

³¹ *Bull. Soc. Ing. Civ. France*, 1923, 76, 620.

³² *Stahl u. Eisen*, 1923, 43, 1095.

power expenditure was measured and complete analysis of the furnace contents, *i.e.*, steel, slag, and furnace gases, was undertaken at intervals. A satisfactory balance was obtained in accounting for the materials with the exception of lime and alumina, with which discrepancies in the weights of added and recovered materials could not be accounted for. The different sources of heat loss were determined. A total thermal efficiency of 62% was obtained, and it is considered that this value could be increased by improving the insulation of the roof by adding loose magnesia as a cover. The electrical efficiency amounted to 60%, the chief source of loss being the transformer loss, on account of the low power factor of the furnace, the value of $\cos \psi$ being as low as 0.35. By the more suitable arrangement of the copper winding of the transformer, it is considered that the electrical efficiency could be increased to 66%.

FERRO-ALLOYS.

An account of improvements in ferro-alloy electric furnaces of high power input is given by B. D. Saklatwalla and A. W. Anderson.³³ Furnaces for this purpose are at present in operation in units of 12,000 kv.-a. capacity. In earlier types it was considered essential to the control of the arc, the bath resistance, and the spacing of the electrodes to avoid too high voltages, and a range of from 40 to 80 volts was generally employed. With the introduction of 60-cycle current, a limit of 3000 kv.-a. capacity was for some time imposed on account of impedance and the serious resistance introduced by skin effect. The results are given of measurements made on the ratio of a.c. to d.c. resistance with leads of different types taking a current of 800 amps. per sq. in. of copper. The reactance voltage drop for all of the systems was then calculated for varying power factors. The results are summarised as follows : (1) The larger the cross-section of the conductor, the larger the skin effect. This effect is appreciable at frequencies of 60 cycles for conductors greater than $\frac{1}{2}$ in. diameter. (2) Skin effect is higher in strips than in tubes of equi-sectional area with consequent higher power loss. (3) Distribution of the current over the sectional area of a conductor is not affected by the inductive disposition of the conductor, since the internal inductance is unaffected by the mutual inductances. (4) Inductive reactance may cause considerable voltage drop in the electrode leads. (5) The larger the diameter of the conductors the less the inductance. (6) The farther apart the conductors the larger the inductance. (7) When inductive reactance expressed as per cent. reactance drop amounts to 20% or more, the actual volts drop in the line increases rapidly with decreased power factor. A description is given of a system of interlaced copper

³³ *J. Amer. Inst. Elec. Eng.*, 1923, **42**, 775.

tube which is employed with delta-connexions with a furnace of 4000 kv.-a. capacity running at 220 volts. By this arrangement slight unbalancing of phases does not materially affect the power factor. Heavy unbalancing, however, sets up impedances at which the power factor falls and leads to a drop in the voltage at the furnace due to reactive inductance, to a greater extent than in the case of interlaced strips. A better protection for sudden overloads is thus provided.

An automatic control is described which maintains a balance on each of the electrodes by means of true watt regulation. Factors in the design and construction of an electric furnace are discussed, which enable a power factor of 99% to be obtained. A new type of electrode holder is described, which enables an electrode to be changed in one to two minutes.

Ferro-Vanadium.

A description is given by E. K. Scott,³⁴ of an electric furnace, which has been designed by B. D. Saklatwalla and A. N. Anderson on the lines described above for the preparation of ferro-vanadium. The input is 4000 kw. three-phase at 220 volts, 60 cycles. The furnace is built of cast-iron segments bolted together, measuring 16 ft. 4 in. long, 12 ft. 8 in. wide, and 7 ft. 10 in. high. The total weight with roof and electrodes is about 80 tons, and the furnace is mounted on rollers so arranged that, when it needs re-lining, it can be rolled away and replaced, a change of furnace being effected in two hours. Two tap holes are provided in the side, one for metal and the other for slag. Round the sides next to the iron there is a layer of fire bricks, inside which is a mass of tamped graphite. The hearth is made of blocks of electrode carbon. In the bottom there are two layers of flint and firebrick, then a thick layer of crushed magnesite, over which graphite is tamped, and finally slabs of carbon. The roof is arched with firebricks set in sections between rectangular pipes, through which cooling water circulates. The electrodes are of graphite, which is chosen in preference to amorphous carbon because of the high current density, namely, 100 amp. per sq. in. The diameter is 12 in., which is the largest commercially available. Before being taken to the furnace each electrode has a copper ring wedged on to it by bronze wedges, and the outside of the ring is tapered to suit the inside of the holder over the furnace. On lowering into the holder, the electrode ring makes a friction contact by its own weight. This arrangement obviates the necessity of conducting any work above the furnace roof. The regulating mechanism by which the electrodes are moved is usually sensitive. The mechanism comprises a watt

³⁴ *Engineer*, 1923, 136, 636.

balance of the Kelvin type, which actuates a contact maker and by means of a special mechanism maintains a phase balance. The conductors which carry current to the electrodes consist of copper tubes which extend through the furnace walls between the transformer house and the furnace room. Flexible cables lead the current from these tubes to copper tubes, which are connected to the electrode holders and carry cooling water. The electrical phenomenon known as "skin effect," is an important consideration when deciding upon the section and arrangements for conductors of currents amounting to 10,000 to 12,000 amps. per phase, especially when at frequencies as high as 60 cycles per second. The conductors are of such a thickness that the current density is about 800 amps. per sq. in. when carrying 12,000 amps. per phase. The tubes are spaced at 7 in. centres and the tubes of each phase are interlaced with those of the other phases; the flexibles are also interlaced. It is arranged that when the furnace is working normally with nearly unity power factor and the phases in balance, the reactance voltage drop is very low. At the same time, if there should be sudden overload, as in the case of a short circuit and unbalancing of phases, then the power factor drops automatically and the reactance voltage is so increased as to protect the plant automatically. A usual furnace charge consists of Peruvian ore, slag from previous runs, carbon, and certain fluxes. All the materials are ground to a fine powder and thoroughly mixed together, and the mixture is fed into the furnace by screw conveyors, and falls through openings in the roof between the electrodes and is fed in continuously. The gases from the furnace are carried off by two ducts, which lead from the top of the furnace to a high chimney. The ferro-vanadium produced contains 35% to 50% of vanadium and is largely used for making tool steel and for the steel framing of motor cars and trucks.

Ferro-Tungsten.

An account is given by K. P. Grigorovitch³⁵ of experiments on the manufacture of ferro-tungsten from Japanese scheelite.

ELECTRIC FURNACES FOR NON-FERROUS METALS.

Electric Brass Furnace Practice.

An exhaustive Report is published by H. W. Gillett and E. L. Mack,³⁶ on the use of electric furnaces in non-ferrous metallurgy. The publication embodies the results of experiments on these types of furnaces conducted by the Bureau of Mines at Cornell University, Ithaca, and also the results of trials made in colla-

³⁵ *Rev. Mét.*, 1923, 20, 183; *J.*, 1923, 458A.

³⁶ *U.S. Bureau of Mines Bull.* No. 202, 1922, 334 pp.

boration with industrial firms, and discusses generally the position with industrial applications of these furnaces. The scope of the enquiry is classified under three headings : (1) Collection of data, for comparison, on the performance of fuel-fired brass furnaces ; (2) experimental work to show whether zinc losses could be reduced by electric melting, without regard to the question of whether or not the type of furnace used was likely to be useful commercially, and (3) attempts to find out, through laboratory tests, inspection of commercial furnaces, attendance at commercial tests, and collection of data, what different types of electric furnaces have done or may be expected to do under various conditions. Not less than 80 different types or different makes of the same type of furnaces have been used, tried, or suggested for melting copper, brass or bronze, aluminium, or nickel alloys.

The general conclusion arrived at is that electric melting gives the advantages expected and usually provides the best and cheapest way to melt brass and many other non-ferrous alloys. It is considered to be only a matter of a few years before fuel-heated furnaces are largely supplanted by electric furnaces for these purposes and electric furnaces will become the standard type for brass melting. The main advantage which is gained by the adoption of electric brass melting is the avoidance of the loss of zinc, which results from volatilisation and oxidation in the case of fuel-heated furnaces. This result is due to the better exclusion of air and furnace gases in the electric furnaces, whereby contamination by sulphur is also avoided. Electric furnaces enable the use of larger units than can be employed satisfactorily with the fuel-heated type. This results in greater uniformity of product, lower labour cost and increased production. Further on account of the cooler and cleaner working conditions, the elimination of much hard manual labour, and the avoidance of zinc fume, the electric furnace leads to an improvement in the comfort, health, and safety of the workmen.

The work of the Bureau also included the laboratory development and semi-commercial testing of the Rocking type of furnace which has been brought into commercial use by the Detroit Electric Furnace Co.

A further account of the operation of the new type of induction furnace developed by the General Electric Co. is given by J. G. Crawford.³⁷ In this design, the melting chamber at the top of the furnace resembles an ordinary crucible underneath which, and communicating with it through ports, is another receptacle in the form of a hollow drum with its axis horizontal. The lower chamber encloses a primary winding, an annulus of the molten metal which forms the secondary of the transformer and connects with the metal

³⁷ *Elect. World*, 1923, 82, 586; also *Amer. Machinist*, 1923, 59, 156.

above, and one arm of a laminated core which passes through the hollow centre of the chamber. When molten, a circulation of the metal takes place between the melting chamber and the heating chamber by the magnetic force of repulsion, which exists between primary and secondary in the transformer. An axial displacement or tilt of the primary relatively to the secondary causes the fluid pressure due to this force to be greater at one end of the secondary cylinder than at the other. Furnaces consuming 75 kw. have been employed for the melting of brass and copper, the holding capacity being 1200 lb. and pouring capacity 750 lb., representing a power consumption, when in continuous operation, not exceeding 220 kw.-hr. per ton.

In the Ryan electric furnace³⁸ which has so far been constructed in units of a holding capacity of 125 lb. of metal, the heat is developed by the passage of a regulated current through a stationary graphite electrode. Temperatures up to 2250° C. are obtained and, in distinction from the arc furnace, an equal diffusion of heat over the whole bath results and superheating is avoided. This feature is of particular advantage in dealing with rare alloys by avoiding oxidation. The furnace is specially adapted for the melting of refractory metals and alloys, such as chromium-nickel-vanadium, and chromium-nickel-tungsten. It is not considered that units of over 500 lb. capacity will become practicable owing to restriction in the size and length of the electrodes and their disposition throughout the furnace. The contacts at the end of the electrodes are cooled by water jackets and attached to bus bars leading to the transformer set placed immediately behind the furnace. The transformers are provided with tapped windings, which are connected with a radial-type switch; this enables a wide range of temperature control to be secured. The furnace is lined with standard magnesite brick, both in roof and hearth, and is either stationary or of the tilting type furnished with a pouring spout. Provision is made, by mounting units of the furnace on trucks, to disconnect one unit and connect a second one within an interval of 5 mins. It is claimed that the consumption of electrodes and power is no higher than that which exists in the best electric melting practice.

In an induction furnace developed by the Compagnie Française de Métaux³⁹ the design is adapted for use with three-phase current and the surface of the metal in contact with the air is reduced to the greatest possible extent. Three magnetic poles are fitted and surrounded by the primary windings while the secondary of the system consists of two concentric rings or channels of rectangular section composed of the molten metal under treatment. The exterior channel communicates at one extremity with the pouring

³⁸ *Chem. and Met. Eng.*, 1923, **28**, 1035.

³⁹ *Le Génie Civil*, 1923, **82**, 207.

spout, while the channel is fed at a point diametrically opposite with the molten metal to be refined. The interior ring connects with the exterior channel, near both the charging and discharging points. The furnace is mounted on a tilting mechanism.

A description is given by A. P. Child⁴⁰ of a 60-kw. brass melting furnace of 200 lb. capacity which was designed and is operated at the University of Wisconsin. The furnace is in the form of a cylindrical drum mounted on runners with axial electrodes and is rocked by a reciprocating mechanism. The speed of working is about one cycle per minute. The shell of the furnace is constructed of sheet-iron and is 28 in. h. ; with a diameter of 30 in. The lining is constructed from fire-sand. Data are given on temperature, output, power consumption, and thermal losses and efficiency.

Tin Recovery from Slags.

A description is given by K. Gottschalk and W. Kroll⁴¹ of experiments made on the reduction of tin from various tin smeltery slags in a 250-kw. electric arc furnace. The furnace was lined with magnesite bricks and was operated at 120 volts. The power consumed was approximately 0·4 kw.-hr. per kg. of liquid slag and 1·1 kw.-hr. per kg. of solid slag. The charges consisted of mixtures of blast-furnace and reverberatory and refinery slags, flue dust, coke, and lime. The product obtained consisted of tin "hard head" containing over 80% of the total tin and copper, together with much iron, some lead and antimony and traces of zinc. The metal was then treated in a converter and the final slag usually contained less than 0·4% of tin.

ALUMINIUM.

An account of recent progress in the aluminium industry is given by Guerin,⁴² who describes recent developments which have taken place in France, in which country a total power consumption of 107,800 kw. is now employed for the production of aluminium. An important factor which applies is the difficulty of the supply of electrodes. It is necessary to import petroleum coke, and resin and pitch which are used for agglomerating the carbon have become more and more scarce since these products are employed in road construction. The electrodes must contain less than 1% of ash and their quality depends not only on the purity of the raw materials, but also on the thorough removal of gas and on their baking, which is now brought about with good results by electric heating.

⁴⁰ Eng. and Min. J., 1923, 115, 278.

⁴¹ Metall u. Erz, 1923, 20, 229; J., 1923, 780A.

⁴² Le Génie Civil, 1923, 82, 455.

The intensity of current in the cells has been increased from 8000 to 20,000 amps., which amounts to a current density of 70 to 80 amps. per sq. foot, and the potential fall is from 7-8 volts per cell. It has been found that aluminium can be efficiently protected against corrosion by air by coating with a very thin layer of hydrogenated cottonseed oil. The local corosions which are sometimes produced with aluminium seem to be rather due to traces of oxides or inclusions in the metal. The presence of aluminium carbide, which forms at comparatively low temperatures, is excluded by avoiding access of gases containing carbon from the metal when molten. Aluminium forms an alloy with iron which is deleterious when present in appreciable amounts. The presence of silicon is useful as a constituent of some aluminium alloys, notably "alpax."

COPPER REFINING AND EXTRACTION.

Recent advances in the technique of the electro-metallurgy of copper are described by Altmayer⁴³ as consisting mainly in improvements which have been made in the use of colloidal and other agents in the purification of the electrolyte and the complete extraction of the precious metals occurring in the anode slimes. An account is given of the general working of the refinery at Great Falls, which was brought into operation in 1918. In this plant a metal is refined which already contains 99% of copper, together with 8.6 oz. of silver and 0.3 oz. of gold per ton. The anode slime remaining from the electrolysis contains, after drying, about 440 kg. of silver and 3 kg. of gold per ton. The daily addition of gelatin for a section of 120 vats may amount to from 280 to 840 grams.

The purification of the main electrolyte is effected as follows : The solution is evaporated down to a density of 48° B. in a special reservoir through which steam-heated coils are passed. It is then led to crystallisation vats, where about 8% of the copper is deposited as sulphate crystals. The solution is then electrolysed in vats with insoluble anodes, whereby the residual copper is deposited together with arsenic, antimony, and bismuth. The impure electrolytic copper thus obtained is returned to the smelting furnaces and added to the copper to be treated at the converters, while the remaining solution is concentrated by boiling up to 56° B., and iron and nickel are extracted in the form of salts. The copper sulphate crystals are employed for preparing fresh electrolyte.

With regard to the direct extraction of copper from ores, two typical examples are given. In one which is operated by the New Cornelia Copper Company, the mineral treated consists of slightly basic oxide and carbonate ores, containing an average of 1.53%

⁴³ *Bull. Soc. Ing. Civ. France*, 1923, 76, 508.

of copper. After leaching with sulphuric acid, the solution is treated in towers with sulphur dioxide, whereby ferric sulphate is reduced to ferrous. The liquor is then electrolysed and made to pass through the same cycle of operations after adjustment of the acid content. The efficiency of this process depends on regulating the content of ferric sulphate which, if too concentrated, leads to the destruction of the linings and lead pipes as well as of the cathodes.

In a process employed by the Chili Copper Co., minerals containing an average of 2·1% of copper and almost entirely free from arsenic, antimony, and bismuth are treated. The ores are dissolved in a solution of sulphuric acid of 8-9% concentration. The solutions are electrolysed with anodes of ferro-silicon, which resist the attack of the residual chlorine.

W. E. Hughes⁴⁴ gives an account of theoretical and practical aspects of the subject of the electro-deposition of copper.

In the Mackay electrolytic process for copper ores,⁴⁵ the sulphide ore is roasted in a specially designed furnace, which enables the temperature and air supply to be accurately regulated so that the copper remains combined as sulphate, while iron and other impurities are converted into basic insoluble salts. The roasted ore is leached with water or spent electrolyte from a previous electrolysis in order to dissolve the copper sulphate until the solution contains about 3% of copper. After leaching, the neutral solution is separated by a filter press and the clear solution mixed with spent electrolyte so that the final solution contains about 2% of copper and from 1·5% to 2% of free acid. This is then electrolysed with a c.d. of about 10 amps. per sq. foot of cathode area until about 50% of the copper in the electrolyte is deposited as metal and the equivalent of sulphuric acid formed. In continuous operation the solution circulates in a closed circuit through the ore on the one side and electrolytic vats on the other until the copper is extracted from the ore and deposited on the cathodes, and the combined acid is regenerated as free acid in the solution. Small amounts of iron and aluminium salts which accumulate in the electrolyte are removed by means of a stream of air, whereby iron is oxidised to ferric salts and precipitated as oxide together with alumina.

A plant using this process has been designed for construction in Australia and will treat 500 tons of silicious ore containing 4% of copper per day.

ZINC.

Electro-thermal Processes.

A comprehensive report on the electro-thermal metallurgy of zinc has been published by B. M. O'Hara.⁴⁶ A review is given of

⁴⁴ Beams, 1923, 12, 19, 92.

⁴⁵ Eng. and Min. J. Press, 1923, 116, 975.

⁴⁶ U.S. Bureau of Mines, Bull. No. 208; J., 1923, 1181A.

the principal work done during the last twenty years on the recovery of zinc from ores by electrical distillation and includes descriptions of the chief patents, with illustrations of the furnaces used as well as extensive excerpts from the technical literature. Special attention is paid to the processes of de Laval, Johnson, Imbert, Thompson and Fitzgerald, Côte and Pierron, Snyder, and Fulton. The difficulties of condensing the zinc vapour are described and the necessity of a well designed condenser is emphasised. The temperature of the gas issuing from the electric furnaces has a tendency to be higher than that from retorts, resulting in the production of excessive quantities of the blue powder. Successful attempts to melt this material by subjecting it to a rubbing action above the melting point of zinc have been made in Scandinavia. The recovery of zinc by electric smelting is higher than that in the retort process, and the cost of retorts and loss of zinc from absorption and diffusion are avoided. Generally a recovery of 90-95% of the zinc should be possible, whilst the lead, copper, and precious metals remain in a residue which is suitable for direct blast-furnace treatment, for their recovery. Again complete recovery of sulphur is not necessary, as iron formed during the process decomposes zinc sulphide, and the ferrous sulphide so produced is not, as in the retort process, detrimental. Given cheap power, electrothermic smelting of zinc ores should be cheaper than either the electrolytic or the retort process.

Electrolytic Processes.

Recent progress in the electrolytic recovery of zinc relate mainly to the systems of purification, circulation, and regeneration of the electrolyte. The main methods at present established for this process are those employed by the Anaconda Copper Company, in which a low current density, *i.e.*, 20-30 amps. per sq. foot, is used and the system of Tainton in which current densities of 100 amps. and upwards per sq. foot are employed. In this case the circulation system is naturally very different, it being necessary to cool the electrolyte effectively and to arrange a more rapid circulation in order to avoid "sprouting," which is followed by short circuits at the electrodes. Amongst other advantages, this process leads to an acceleration in the production which entails an economy in the capital outlay and overhead charges incurred by the plant and materials.

The extraction of zinc is now the most important electrolytic process after that of copper. The general conditions necessary to its economy may be defined as the availability of large quantities of ore of an adequate metal content, the amount of silica to be not too high, and the composition of the ore to be sufficiently constant to avoid modifying the routine in the preparation of the zinc solution

for electrolysis. The process is suitable for complex ores which cannot be economically treated by smelting methods.

An account is given by J. O. Betterton⁴⁷ of experiments made on the direct leaching of zinc ores with sulphuric acid and the subsequent extraction of the zinc by electrolysis. The ore contained relatively large quantities of soluble silica, also vanadium. These substances were precipitated from the acid leach solution and removed by a filter-press. The filtrate was treated with zinc dust before going to the cells for electrolysis. Considerable trouble was found with the separation of gelatinous silica from the slightly acid silicate solution used for the leaching. The main factors affecting the formation of this gel were found to be the concentration of zinc and of free acid. The higher the concentration of these substances the shorter the interval which elapsed before gel formation. With increasing content of silica, the time interval preceding incipient gel formation is shortened as the silica is increased from 8 to 10 g. per litre and then rapidly increases when the silica content increases from 10 to 13 g. per litre. A method of removing the silica from solution in a filterable and washable form is developed and consists in making the solution alkaline by the addition of zinc oxide fume. By adding 5 lb. in excess of zinc oxide to 2 tons of solution containing 1% of silica and 5-8% of zinc and heating to a temperature of 90°-100° C., the silica is nearly all removed in less than one hour; 1-2% of the total silica still remains, however, and is precipitated during the zinc dust treatment. The silica separates rapidly from the first, but until precipitation is practically complete the clear supernatant solution will not pass through a filter paper. The precipitated silica filters and washes readily after the reaction is ended, the gelatinous condition occurring with the dissolved silica which is in the transition stage.

A method is devised by S. Field and W. E. Harris,⁴⁸ in which use is made of the Al-Hg or Zn-Hg couple in eliminating impurities from the slightly acid solutions obtained from the leaching of the ore. These solutions are first freed from iron and nickel. Mercuric sulphate is then added followed by zinc powder or zinc blue. The more electro-positive metallic impurities are deposited, while the evolution of hydrogen is prevented by the high overvoltage on the surface of the alloy formed. Economy of zinc is effected by this method and the process becomes applicable also in cases in which high acid content would prohibit purification owing to high consumption of zinc. An estimate of the costs of the purification chemicals is included.

An investigation of the chemical, physical, and mechanical properties of electrolytically deposited zinc from sulphate solution

⁴⁷ Eng. and Min. J., 1923, 116, 67.

⁴⁸ Trans. Amer. Electrochem. Soc., 1923, 269 (Advance Copy); J., 1923, 1075A.

has been made by M. von Schwarz.⁴⁹ The metal obtained is of about 99.9% purity. It is observed that during the electrolysis zinc crystals are deposited in directions normal to the cathode surface. A peculiar ring structure is exhibited by sections parallel to the latter. Electro-deposition occurs most readily at angles, corners, and rough parts of the cathode. The brittleness of electrolytic zinc is attributed to the presence of hydrogen, which, in the case of the sample investigated, was found to be present to the extent of 0.055%. When electrolytic zinc is melted the hydrogen flame can be observed. When heated to 105°–110° C. for some hours a loss of weight of 0.025–0.04% occurs. A plate of zinc so treated becomes curved slightly and a considerable volume of hydrogen is evolved. When heated to a temperature above 180° C. the plate becomes very curved, the concavity being directed towards the original cathode surface. The phenomenon is accompanied by a decrease of 0.7 in the density of the metal. The electrical conductivity of electrolytic zinc is practically the same as that of pure zinc, but the value at 195°C. is much below the anticipated value. This decrease and the decrease of density occurring at about the same temperature are not reversible phenomena, but are connected with the evolution of hydrogen. Determinations of hardness at high temperatures are in agreement with the customary values. Very little, if any, hydrogen is dissolved in electrolytic zinc or electrolytic iron which has been stored for a long period.

An extended investigation is made on the electrolytic extraction of zinc from Swedish ore by means of the Siemens und Halske process by W. Palmer and A. Wejnarth.⁵⁰ The relative merits of the use of chloride and sulphate solutions are compared and the latter is found preferable. In continuous operation, one half of the zinc is extracted from a given electrolyte before regeneration with an average current efficiency of 75%. By employing a current density of 25 amps. per sq. foot of cathode and an average voltage of 3.5, a deposit 3 mm. thick is obtained in four days. A discussion is given of the methods of roasting and leaching the ore, the purification of the solution, and the specific influence of different impurities present on the deposited metal. With regard to colloidal additions to the electrolyte, it is found that no marked advantage is obtained by the presence of small amounts of glue and its use is not recommended. The anodes used are of electrolytic lead and their consumption, which is mostly recovered in the form of disintegrated metal and oxide, amounts to 0.8–1% of the weight of zinc deposited. Aluminium is found to be most suitable for the cathode starting sheets. A useful property is the passivity which this metal assumes in the acid electrolyte. The deposited metal is in a state of strain

⁴⁹ Z. Elektrochem., 1923, 29, 198; J., 1923, 807A.

⁵⁰ Ibid., 1923, 29, 557.

which causes the zinc to become bent without, however, cracking. This effect diminishes the adhesion of the metal to the cathode and thus facilitates its separation.

An investigation is made of the crystalline form of the electro-deposited zinc by means of X-ray analysis. The theory which assumes a transition from amorphous to a crystalline form on standing is rejected and it is considered that a recrystallisation occurs in accordance with Tammann's theory. The changes of resistance and electrode potential during the electrolysis are measured. An opinion is given on the economic outlook for the electrolytic extraction of zinc compared with electrothermal methods. It is estimated that a power expenditure of 0.8 kw.-year per ton of zinc is needed in electrothermal treatment compared with 0.45 kw.-year per ton by the electrolytic process.

IRON.

An account is given by H. D. Hineline⁵¹ of experiments which were carried out to determine the type of plating bath that would give good deposits of iron on to irregularly-shaped rubber articles. A conducting coating on the rubber is easily obtained by varnishing it, and then brushing in graphite. After trying various compositions, good heavy deposits up to $\frac{1}{2}$ -in. in thickness and high throwing power to ensure filling the crevices were obtained with an electrolyte of ferrous and calcium chlorides, containing chromous chloride and quinol as reducing agents. The best results were obtained with current densities of 25-75 amps. per sq. foot and temperatures between 60° and 70° C. The solution should contain from 0.01% to 0.5% of free acid to prevent the precipitation of ferrous hydroxide or ferrous carbonate.

CADMIUM.⁵²

The sources of cadmium are the precipitates obtained by the addition of zinc powder in preparing a zinc sulphate electrolyte, or the fumes and dust disengaged in zinc or lead smelting, which are collected in dust chambers or filters. Cadmium is extracted at two factories in America. In one at Kennett, the raw material, which contains only 0.55% of cadmium, is treated with sulphuric acid, chalk is added and at the same time the material is oxidised by subjecting it to a current of air, whereby iron, arsenic, and about half of the copper are precipitated. On the addition of zinc powder a precipitate is obtained containing 25% of cadmium. The subsequent operations consist in lixiviation by sulphuric acid, separation of the solution and the residue of copper, precipitation of cadmium in the form of spongy metal, solution of cadmium in an

⁵¹ *Trans. Amer. Electrochem. Soc.*, 1923, 43, 21; *J.*, 1923, 185A.

⁵² Altmayer, *loc. cit.*

acid electrolyte, elimination of iron, and thallium, if present, and electrolysis with rotating aluminium cathodes. The presence of arsenic involves a modification of the routine in order to remove this element as AsH_3 . In works at Midvale, a material containing 15% of cadmium, 20% of lead, and 50% of arsenic is treated. The product is roasted, leached, treated in a reverberatory furnace again leached, and after neutralisation of the solutions by lime to remove the remaining impurities, the filtered liquor is subjected to electrolysis. It is necessary to avoid the presence of iron or raising the temperature, which encourage solution of the cadmium at the cathode.

LEAD.

The method universally adopted in lead refining is the Betts process; the anodes should contain not less than 98% of lead; the most harmful impurities are tin and tellurium. The electrolyte consists of lead fluosilicate and free hydrofluosilicic acid. The system of electrolysis and arrangement of vats are similar to those employed in the refining of copper. The c.d. employed is 18 amps per sq. foot; temperature 37° — 38° C.; the quantity of gelatir added is carefully regulated and amounts to about 1 kg. per ton of lead deposited. It is necessary that the slimes should adhere to the anodes as their collection at the bottom of the vats would form a conducting layer. The adhesion is assisted by the presence of arsenic and antimony (together amounting to about 0·6%). These slimes contain 10–15% of lead, 35–40% of antimony, 5–10% of bismuth, 15–16% of precious metals. It may be taken, in general that the Betts process is not suitable for impure lead. With a low price for power and skilled attendance, the Betts process can often compete with that of Parkes.

TIN.

The amount of tin produced is small compared with other metal and its electrolytic recovery is limited to special cases. It has been applied and found remunerative in America on account of the recovery of precious metals which cannot be achieved with a good yield by ordinary processes. The tin content of the anode varies from 96% to 98%; the electrolyte is a fluosilicate of tin prepared in the vats themselves. In the process of Whitehead, the cathode is protected by a porous vase and an electrolyte containing 20% hydrofluosilicic acid and 0·1% of sulphuric acid is employed. The function of the sulphuric acid, the amount of which should be held constant, is to precipitate lead, which is a harmful impurity. It is further necessary to avoid the presence of iron. The c.d. is about 18 amps. per sq. foot, and the temperature of the electrolyte is kept below 20°C . in order to avoid the decomposition of hydrofluosilicic acid into silicon fluoride.

NICKEL.

The Hybinette process which was developed in Norway has been improved and applied on a large scale by the British American Nickel Corporation, Ltd. The characteristic features of the American process are the production of a matte with 56% Ni and 24% Cu; after grinding and roasting at a low temperature, this is leached with a solution of sulphuric acid whereby part of the copper is dissolved and a solution given containing 4.5% Cu, 0.8% Ni, and 1% of free acid, which forms the electrolyte. The residue from the leaching is dried, melted, and formed into anodes containing 80% Ni, 18% Cu, and 2% Fe. The electrolysis, conducted at first with soluble copper anodes, gives copper on the cathode until the content of this metal in the electrolyte is lowered to 1.5%. The content of the nickel in the electrolyte is increased and that of the copper lowered by continuing the electrolysis with soluble nickeliferous anodes, when some of the copper is displaced by solution of the nickel. The electrolysis is then continued with the use of insoluble anodes of antimonial lead, when with a c.d. of 250 amps. per sq. foot, the addition of gelatin, and the use of a temperature of 75° C. Ni is deposited. The electrolyte is cooled and nickel sulphate crystallised out and dissolved to form fresh electrolyte. The acid mother liquor is employed for leaching matte. The essential point of the process consists in controlling the proportions of nickel and copper in the matte. In this process the losses of copper and nickel are small and practically the whole of the precious metals are recovered.

SILVER.

A description is given by A. H. W. Cleave⁵³ of a cell which has been developed at the Ottawa Mint for the electrolytic refining of silver which enables a greater output than with the Möbius cell. The crude silver containing 10-16% of base metal is cast into anodes. The cells employed are annular, 36 in. in diam., and provided with a hollow centre in which is situated the support for the cathode carrier. The electrolyte is contained in the annular space between the outer and inner walls of the cells. This space is 8 in. wide and 18 in. deep. The cathodes rotate at a peripheral speed of 40 feet per min., which serves to keep the electrolyte well mixed and to prevent any tendency to stratification. The c.d. may range from 75 to 150 amps. per sq. foot without unduly increasing the temperature of the electrolyte or fouling it or increasing the resistance of the cell abnormally. The working voltage of the cell does not exceed 1.2 volts at 75 amps. or 2.5 volts at 150 amps. per sq. foot of cathode area. The highest temperature of the

⁵³ Eng. and Min. J., 1923, 116, 21.

electrolyte at 75 amps. is 30° C., and 40° at 150 amps. when in continuous operation. By means of specially designed cathodes, and multiple grouping of the anodes, the current becomes a pulsating one, which causes the deposited silver to adhere loosely to the cathodes so that it is easily removed. The cathodes are automatically stripped by means of a scraper, which can be adjusted so as to keep the spaces between the anode and cathode faces constant. The silver stripped from the cathodes falls into removable trays, which are emptied at intervals of about four hours. The deposited silver is dense and crystalline and is of a purity of 99.90–99.99%.

MANGANESE.

An account of some properties of electrolytic manganese is given by A. N. Campbell.⁵⁴ Determinations were made of the density and chemical properties of the metal and the results of potential measurements in salt solutions are detailed.

GENERAL.

A theory of the mechanism of crystal formation in electro-deposition is outlined by W. Blum and H. S. Rawdon.⁵⁵ The principal types of crystalline structures observed in electro-deposits are classified and the conditions which tend towards the formation of the different types are discussed.

An account is given by H. E. Haring and W. Blum⁵⁶ of the current distribution and throwing power in the electro-deposition of metals.

In an article on the corrosion of electrolytic iron by W. E. Hughes⁵⁷ it is concluded that the properties of electrolytic iron depend largely on the nature of the solution used for its production. The differences are attributed to the effect of inclusions of salts in promoting corrosion.

The conditions which affect the electrolytic deposition of chromium are outlined by E. Liebreich.⁵⁸

An article on the chromium-plating of steel by using chromium anodes is published by K. W. Schwartz.⁵⁹

⁵⁴ *Chem. Soc. Trans.*, 1923, **123**, 2323; *J.*, 1923, 1133A.

⁵⁵ *Trans. Amer. Electrochem. Soc.*, 1923, 247 (*Advance Copy*); *J.*, 1923, 1076A.

⁵⁶ *Ibid.*, 365 (*Advance Copy*); *J.*, 1923, 556A.

⁵⁷ *Chem. and Met. Eng.*, 1923, **29**, 536; *J.*, 1923, 1074A.

⁵⁸ *Z. Elektrochem.*, 1923, **29**, 208; *J.*, 1923, 607A.

⁵⁹ *Trans. Amer. Electrochem. Soc.*, 1923, 13 (*Advance Copy*); *J.*, 1923, 891A.

OILS, FATS, AND WAXES.

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GENERAL.

It does not appear that any very rapid or far-reaching advances have been made during the period under review in either the science or the technology of oils and fats, but it is certain that in both steady progress has been made.

In the trade in oilseeds, oils, and allied products there are few points worthy of special comment; conditions appear to be gradually becoming more stable and the prices of raw materials have been more on a normal basis.

One curious feature of the trade in oils has been the relation between the price of "acid oil" and the crude oil from which it is derived as a by-product of the removal of free fatty acids by neutralisation; for a long time past the prices of "acid oils" have remained at a figure very close to the price of crude oils—an occurrence which can only be considered abnormal, as in the past "acid oils" have frequently been quoted at about half the price of the crude oils, and even at this low price have not been easy to dispose of. The reason for the present relationship in price is not easy to decide. It is probably due—in part at any rate—to the control of glycerin prices by trade monopoly, and to the smaller demand for glycerin under peace conditions.

It may be said with some justice that full realisation of the value and uses of margarine was a lesson only taught by the war. Although margarine is now obtainable at practically the same prices as those ruling in pre-war days, manufacturers of margarine in this country are passing through difficult times, owing partly to over-production (and to the present lower price of, and the preference for, butter), but mainly to a short-sighted policy of competitive price-cutting. If it is found possible in the future to obviate the lack of vitamins in margarine and so to make margarine fully equal in dietetic value to butter, perhaps this essential industry may receive a fresh impetus.

A point which cannot fail to strike those interested in the oil industry is the small extent to which vegetable fats of the "vegetable lard" type are used in Great Britain compared with America; vegetable fats are, of course, used to a very large extent in several industries in this country, but the domestic use of vegetable fats is comparatively small, though there is some evidence that attempts

are being made to develop the use of these materials, and there is certainly room for expansion.

The increased demand for palm oil in the United States of America is a feature of some interest, particularly as palm oil is such an important product of our West African possessions. Although West Africa, and particularly British West Africa, is the natural habitat of the oil-palm, its cultivation in plantations in the Dutch East Indies, chiefly in East Sumatra, has been extremely successful during the last few years, where the oil-palm has proved very responsive to efficient cultural methods, yielding fruit at an earlier age than in West Africa, and producing larger yields. According to, E. Fickendey,¹ Sumatra oil-palm fruit contains more gum and also more moisture than African fruit, so that in pressing the Sumatra fruit a turbid oil is obtained and more oil remains in the residue.

The future of the oil-palm in the East is a matter of considerable interest and importance, and it seems highly desirable that research on the cultivation and exploitation of the tree in British West Africa should receive the immediate and close attention of the Governments concerned. The oil-palm has been found to do well in some of our British possessions in the East, notably Malaya, where it seems likely that large areas will be cultivated in the near future.

In the scientific investigation of oils, fatty acids, and soaps it is gratifying to see that many workers are carrying out researches and applying the most modern methods known to physics and chemistry, such as the application of X-rays to the elucidation of the structure of the fatty acid molecule and the consideration of the effects of the colloidal state in soap and soap solutions. The methods of isolating, identifying, and synthesising the many fatty acids are being gradually developed. One of the few problems which does not seem to have received so much attention as it deserves (see p. 311) is the separation and determination of the mixed glycerides, which are of particular interest and importance in edible fats ; this is a problem which it will obviously be difficult to solve, but which cannot be regarded as incapable of solution, especially when one considers the great progress already made in such difficult problems as are encountered in separating mixtures of fatty acids. This problem was referred to at some length in the last Report,² but no apology need be made for again calling attention to it here in the hope that workers may be induced to attempt its solution.

It is of interest to note in connexion with mixed triglycerides that the possibility of manufacturing them artificially has not

¹ *Kolloid-Zeits.*, 1923, **33**, 107 ; *J.*, 1923, 895A.

² *Ann. Repts.*, 1922, **7**, 279.

been overlooked; G. Schicht and A. Grün have proposed to effect this by esterification of mono- and di-glycerides with fatty acids.³

Rancidity is a problem, and a serious one, particularly for the edible oil manufacturer, and although it cannot yet be claimed that all the causes of rancidity are known, steady progress is being made.

The deterioration of mutton and beef fats has been investigated by J. F. Bevis,⁴ who found that the action of light greatly accelerated the decomposition of fats at ordinary temperature, and that free oleic acid increased the rate of formation of substances reacting in the Kreis test, while free glycerol had no effect. The increase in free fatty acid bore no relation to the Kreis test. For the detection of rancidity this author considers the Kreis test more sensitive than the Issoglio oxidation method. The natural colouring matter appeared to play some part in the decomposition of fats.

The Kreis test is also recommended by R. H. Kerr and D. G. Sorber,⁵ who discuss the causes of and phenomena associated with rancidity, and its influence on analytical characteristics.

A new test for acrolein and its bearing on rancidity has been described by W. C. Powick.⁶ Acrolein and phloroglucinol form in presence of hydrogen chloride and hydrogen peroxide a deep red product showing a well-defined absorption band in the yellow-green region of the spectrum, which is spectroscopically identical with that obtained in the Kreis rancidity test.

On the more purely technical side several interesting papers have been published. The extraction of oils by solvents has, of course, been carried out for many years on a very large scale in this country and elsewhere. In the opinion of E. W. Albrecht⁷ petroleum spirit is the best solvent, and the process has advantages over expression in labour, steam and power consumption; the loss of solvent is below 1% in modern plant, when efficiently worked, while the oil content of the meal may be reduced to 1% and no difference in quality between expressed and extracted oils can be detected. This last statement is true in many cases, but certainly not in all; extracted oils are in some cases even superior to expressed oils, but a good many factors, such as consideration of the subsequent use of the oil, to mention only one, must be taken into account in comparing an extracted oil with an expressed oil.

Although there are several efficient extraction plants on the market, a good deal of attention is apparently being given to the

³ E.P. 160,840; *J.*, 1922, 945A.

⁴ *J.*, 1923, 417r.

⁵ *Ind. Eng. Chem.*, 1923, 15, 383; *J.*, 1923, 563A.

⁶ *Ibid.*, 1923, 15, 66; *J.*, 1923, 376A.

⁷ *Chem.-Zeit.*, 1922, 46, 1034; *J.*, 1923, 22A.

production of plant of greater efficiency, particularly towards designing plant for continuous instead of intermittent extraction. In the expression of oil from seeds a continuous process would be an obvious advantage in many ways, and ingenious plant for attaining this end has been patented recently by A. E. Culley.⁸ Space will not allow of any detailed description of the process being given here, but it consists briefly in subjecting the oil-containing material to pressure between a metallic belt or belts passing between rollers, when the oil is forced to the edges of the belt and collected. Trials have been made recently, the results of which are believed to be most satisfactory, and the results of working this process continuously under actual manufacturing conditions will be of great interest when available.

An interesting contribution to the refining of edible oils has been made by B. H. Thurman,⁹ who discusses the losses due to impurities in the oil and caused by subjecting it to neutralisation, decolorisation, hardening, and deodorising. The results noted are of particular value as they were obtained under actual working conditions with large quantities of material. The author states that the substance which Hulme found to be precipitated from cotton-seed oil by treatment with boric acid is a phosphatide, and discusses the losses occasioned by this substance.

The importance of fuller's earth as an agent for decolorising oils is common knowledge, though little is known as to why certain types of earth are more effective than others, or why their action varies on different kinds of oil. It is true that the problem has in the past been the subject of a good deal of theorising without, to put it plainly, sufficient experimental proof, and it is gratifying to note that two communications have been published recently. E. K. Rideal and W. Thomas¹⁰ have examined three types of fuller's earth, and have determined the specific surface, the adsorption of methylene blue, and the power of catalytically decomposing hydrogen peroxide. They found that the adsorption of methylene blue from aqueous solutions was approximately proportional to the specific surface, but that the catalytic power of decomposing hydrogen peroxide was not connected with surface or adsorptive power for methylene blue, and suggest that the oil-decolorising properties are connected with the powers of adsorption and catalytic oxidation, and that the latter property is related to the iron content of the earth. With no wish to be hypercritical, one cannot refrain from suggesting that this interesting piece of research might have been pushed further and have included actual work on oils. A

⁸ E.P. 201,190; J., 1923, 938A.

⁹ Ind. Eng. Chem., 1923, 15, 395; J., 1923, 561A.

¹⁰ Chem. Soc. Trans., 1922, 121, 2119; J., 1922, 981A.

publication by D. Wesson¹¹ deals with some most interesting results obtained in decolorising cotton-seed oil with various earths, but is also incomplete. The results clearly demonstrate that oil retained by the earth is in an oxidised condition due to the action of the earth on the oil, but the fact that the best decolorising earth, which gave the highest adsorption, showed the least effect in oxidising ferrous sulphate, is sufficient evidence that further work is greatly needed on this interesting problem; in fact the author says, "the object of this paper is to call attention to some unpublished observations which may assist others eventually to solve the problem," and I must agree that the publication of an incomplete research such as this is an act of generosity on the part of the worker and more suggestive and valuable than much completed work. The oxidising effect of decolorising earths is also referred to by B. H. Thurman,¹² who notes that carbon does not appear to produce the effect.

The work on vitamins is progressing steadily, and there is now no doubt that the chief cause of infantile rickets is a lack of vitamins associated with certain oils. The researches of Miss Chick and her co-workers¹³ have established that sunlight or other radiations of short wave-length enable animals to economise the supply of vitamins. Larger supplies of vitamin A must therefore be supplied to prevent rickets if the subject is exposed to bad conditions of lighting. In investigating the effect of short wave-length radiations on economising or activating the vitamin A, E. M. Hume and H. Henderson have made the interesting discovery that direct exposure of the animal to the rays is not necessary, but that the same effect may be produced by merely placing the animal in a vessel containing air previously irradiated; the explanation of this discovery must be awaited with considerable interest.

The subject of vitamins will be found more fully discussed under the section on "Foods."

DRYING OILS.

An interesting contribution to the study of the drying of linseed oil has been made by F. H. Rhodes and A. E. Van Wirt,¹⁴ who have investigated the action of various pigments on the rate of oxidation of oil. Their results support the theory that the drying of oil is an autocatalytic reaction, the catalyst being an oxidation product of the oil itself. Lead salts act as pseudo-catalysts by promoting the formation of such oxidation products and do not have a marked effect on the total oxygen-absorption of the oil.

¹¹ *Cotton Oil Press*, 1923, 7, No. 6, p. 28.

¹² *Ind. Eng. Chem.*, 1923, 15, 396; *J.*, 1923, 56A.

¹³ *Medical Research Council, Special Report*, No. 77, 1923; *Chem. and Ind.*, 1923, 811.

¹⁴ *Ind. Eng. Chem.*, 1923, 15, 1135; *J.*, 1923, 1233A.

Pigments often have a considerable influence on the rates of absorption of oxygen and of evolution of oxygen absorbed and volatile matter evolved. For instance, leaded zinc, lithopone, "titanox," and barium sulphate all retard oxidation and evolution of volatile matter, and also reduce the amounts of oxygen absorbed and volatile matter given off. This effect seems to be due partly to the fact that the oil hardens at an earlier stage when mixed with pigments.

Zinc white appears to be somewhat capricious in its effects; in some cases it acts as an inert filler, decreasing the initial speed of oxidation without affecting the amounts of oxygen finally absorbed or evolved, whilst in other cases it resembles lithopone and leaded zinc in action, causing rapid hardening of the oil and decreasing oxygen absorbed and volatile matter evolved. This paper contains the results of a large number of detailed experiments which should prove valuable to paint and varnish manufacturers.

A comparison of linseed oils produced in the United States of America with imported oils has been made by H. A. Gardner¹⁵; oil imported from Europe (produced from Argentine seed) has an iodine value below 180, oil from Japanese or Calcutta seed has an iodine value around 180, and Canadian and North American oil has an iodine value of 182-186. Analytical data obtained in the examination of a large number of commercial linseed oils have also been described and discussed by H. Wolff.¹⁶ The presence of two phytosterols in linseed oil has been recorded by R. J. Anderson and M. G. Moore.¹⁷

The commercial importance of tung (Chinese wood) oil appears to be increasing as its technical value becomes more generally recognised. It is to be hoped that serious attempts will be made to grow this oilseed in British possessions as has already been done in the United States of America. At present this country is entirely dependent for supplies on the East, though the importance of the oil was recognised and the desirability of attempting to grow the tree in British possessions was pointed out some years ago.

J. Marcussen¹⁸ states that when exposed to light in absence of air tung oil changes into a solid, which may be separated by treatment with acetone into a soluble fraction—mostly unchanged oil—and an insoluble fraction consisting of β -elæostearin (m.p. 61° C. after purification); a small quantity of infusible substance insoluble in all fat solvents is also formed. The formation of β -elæostearin from α -elæostearin is an instance of stereoisomeric

¹⁵ *Circ.*, 158, U.S. Paint Manuf. Assoc., 1922; *J.*, 1923, 22A.

¹⁶ *Chem.-Zeit.*, 1923, 47, 142; *J.*, 1923, 275A.

¹⁷ *J. Amer. Chem. Soc.*, 1923, 45, 1944; *J.*, 1923, 937A.

¹⁸ *Z. angew. Chem.*, 1922, 35, 543; *J.*, 1922, 866A. *Z. Deuts. Oel- u. Fettind.*, 1923, 43, 162; *J.*, 1923, 938A.

re-arrangement from the *cis*- to the *trans*-form. In contact with air or exposed to light in a sealed tube the oil polymerises to a product insoluble in fat solvents.

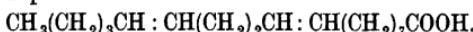
Raw tung oil dries with formation of gelatinous masses of β -elæostearin and the dried film lacks durability; by heating the oil polymerisation is brought about so that on drying β -elæostearin is not formed and the oil is rendered suitable for paints.

Substances, such as linseed oil and colophony, which prevent coagulation on heating do so by reducing the tendency of the sol to pass to the gel form.

The behaviour of tung oil on heating in comparison with linseed has been studied by C. F. Mabery.¹⁹

The decrease in refractive index of tung oil has been found by F. H. Rhodes and H. E. Goldsmith²⁰ to be 0.000395 for each 1° C. rise in temperature.

According to A. Vercruyssse,²¹ the products of oxidation of elæomargaric acid and the products of decomposition after ozonisation point to the formula



The analytical characters of the oils from four species of *Aleurites*, *A. cordata*—Japanese tung; *A. Fordii*—Chinese tung; *A. montana*—Kangtong tung; and *A. moluccana*—Bakoly, have been determined by I. Miura.²²

The unsaturated fatty acids from perilla oil have been studied by K. H. Bauer²³ and found to contain oleic acid; the linolenic acid from perilla oil gave the same hexabromostearic acid as is obtained from linseed oil, but linolenic acid from perilla oil gave on oxidation only small amounts of linusic and isolinusic acids, together with an isomeric hexahydroxy acid not obtained from linseed oil; linolenic acid obtained by debromination of hexabromostearic acid was not identical with the acid originally brominated. The authors maintain that it is unsafe to draw conclusions as to the presence of isomeric linolenic acids from the behaviour on bromination alone.

SEMI-DRYING AND NON-DRYING OILS.

The composition of soya bean oil has been submitted to detailed investigation by W. F. Baughman and G. S. Jamieson²⁴ with the following results:—glycerides of fatty acids: linolenic 2.3, linolic 57.5, oleic 33.4, palmitic 6.8, stearic 4.4, arachidic 0.7, lignoceric

¹⁹ *Ind. Eng. Chem.*, 1923, 15, 365; *J.*, 1923, 563A.

²⁰ *Ibid.* 1923, 15, 786; *J.*, 1923, 938A.

²¹ *Bull. Soc. Chim. Belg.*, 1923, 32, 151; *J.*, 1923, 665A.

²² *Kogyō-Kwagaku Zasshi*, 1923, 26, 316; *J.*, 1923, 786A.

²³ *Chem. Umschau*, 1923, 30, 9; *J.*, 1923, 149A.

²⁴ *J. Amer. Chem. Soc.* 1922, 44, 2947; *J.*, 1923, 149A.

0·1% ; unsaponifiable matter, 0·6% ; saturated acids, 11·5% ; unsaturated acids, 83·5%.

The same authors have examined sunflower seed oil²⁵ which consisted of glycerides of fatty acids : linolic 57·5, oleic 33·4, palmitic 3·5, stearic 2·9, arachidic 0·6, lignoceric 0·4% ; unsaponifiable matter 1·2% ; saturated acids, 7·1% ; unsaturated acids 86·6%.

The acetyl value of grape seed oil is stated by E. André²⁶ not to be due to the presence of ricinoleic acid, but to the presence of hydroxy acids of lower molecular weight containing 14 to 16 carbon atoms, and at least two hydroxy acids, one saturated and the other unsaturated, appear to be present.

In agreement with Gill and Tuft,²⁷ phytosterol was found by R. J. Anderson and M. G. Moore²⁸ to be the chief constituent of the unsaponifiable matter of maize oil, while stigmasterol was absent. Cotton-seed oil contained at least two phytosterols, the separation of which by fractional crystallisation was very difficult.

Rape oil derived from Japanese rape seed (*Brassica campestris*. L., *B. Chinensis*) was found by Y. Toyama²⁹ to contain about 65% of erucic acid ; saturated acids were present to the extent of less than 2%, and from these palmitic acid was isolated, while stearic, behenic, lignoceric, and arachidic acids were probably present ; indications of linolic and oleic acids were also obtained. The lead salt ether and lead salt alcohol methods of separation of fatty acids were found unsuitable for rape oil. Several derivatives of erucic acid and of behenic acid (prepared from erucic acid by hydrogenation) were prepared and characterised³⁰ ; these data will no doubt prove useful aids in the identification of the above fatty acids.

By shaking a 50% solution of a crude vegetable oil in petroleum ether with copper acetate, all crude oils, except cotton seed oil, develop a pale to dark emerald-green colour ; no colour is produced with refined oils. W. W. Dickhart³¹ suggests that this test is useful for the differentiation of crude kapok and cotton seed oils, or, by using a tintometer, for the detection of as little as 0·5% of crude vegetable oils in cotton seed oil. The value of this test appears to be rather problematical as crude cotton seed oil is not very likely, owing to its comparatively low value, to be adulterated with other oils, while refined oils apparently do not react, and addition of crude oils to refined cotton oil is highly improbable.

²⁵ *J. Amer. Chem. Soc.*, 1922, **44**, 2952 ; *J.*, 1923, 140A.

²⁶ *Comptes rend.*, 1923, **176**, 843 ; *J.*, 1923, 410A.

²⁷ *J.*, 1903, 501.

²⁸ *J. Amer. Chem. Soc.*, 1923, **45**, 1944 ; *J.*, 1923, 937A.

²⁹ *Kogyō-Kwagaku Zasshi*, 1922, **25**, 1044 ; *J.*, 1922, 988A.

³⁰ *Ibid.*, 1053 ; *J.*, 1922, 988A.

³¹ *Amer. J. Pharm.*, 1923, **95**, 108 ; *J.*, 1923, 317A.

The detection of arachis (ground nut) oil and its determination in mixtures is a problem which has already received a good deal of attention. According to A. W. Thomas and C. L. Yu³² separation of stearic, arachidic, and lignoceric acids may be effected by means of their magnesium salts, which are only slightly soluble in 90% (by vol.) alcohol, while the magnesium salts of oleic, linolic, and linolenic acids are easily soluble. The behaviour of the insoluble magnesium salts obtained from rape and tung oils has also been studied.³³

MARINE ANIMAL OILS.

The methods of manufacture of cod liver oil employed in Newfoundland have been investigated by S. S. Zilva and J. C. Drummond.³⁴ The manufacture of oil is under the control of the Ministry of Marine, the direct steam process being almost exclusively used; the oil produced is of very high and uniform vitamin potency.

Pilchard oil (from *Clupea pilchardus*), of which 60,000 gallons was produced at Cornish fishing stations in 1921 from the pilchards pickled for export, has been examined by H. M. Langton.³⁵ The physical and chemical characteristics of two samples of oil are given, together with information as to the nature of the oil and character of the soap produced. The oil contains clupanodonic acid and appears to be chiefly employed in soft soap manufacture.

On separation of the unsaponifiable matter of cod liver oil, by saponification with alcoholic potash and removal of fatty acids as calcium salts, K. Hattori and T. Obata³⁶ obtained a product having from five to ten times the vitamin potency of the original oil. The liver oil of *Squalus acanthias* is stated by S. Berlingozzi and M. Tomasini,³⁷ closely to resemble cod liver oil; it contains 1.1% of squalene, and 2.9% of cholesterol etc., and hydrogenates readily. The saturated hydrocarbon iso-octadecane, $C_{18}H_{38}$, isolated from the liver-oil of the giant shark (*Cetorhinus maximus*, Gunner) by M. Tsujimoto, has been found by G. Toyama³⁸ to be present in the liver-oils of three other species of shark. This hydrocarbon appears to be present generally in liver oils containing squalene, and the author proposes to name it pristane.

In continuation of his already voluminous work on liver oils, M. Tsujimoto³⁹ gives the results of examination of the oils of the

³² *J. Amer. Chem. Soc.*, 1923, **45**, 113; *J.*, 1923, 232A.

³³ *Ibid.*, 129; *J.*, 1923, 233A.

³⁴ *J.*, 1923, 185T.

³⁵ *J.*, 1923, 47T.

³⁶ *Yakuga-Kuzasshi*, 1923, No. 497, 525; *J.*, 1923, 987A.

³⁷ *Annali Chim. Appl.*, 1923, **7**, 29; *J.*, 1923, 561A.

³⁸ *Chem. Umschau*, 1923, **30**, 181; *J.*, 1923, 840A.

³⁹ *Ibid.*, 1922, **29**, 385; *J.*, 1923, 104A.

"ishinagi" (*Stereoypsis ischinagi*) and the "abura-bodzu" (*Erelepis zonifer*, Lockington). The same author has also isolated⁴⁰ a tetradecylenic acid, $C_{14}H_{26}O_2$ (probably the $\Delta 9$ compound) from sperm oil (3·0%) and dolphin head oil (0·4%).

The composition of menhaden oil has been investigated by J. B. Brown and G. D. Beal,⁴¹ who have attempted the separation of the fatty acids, particularly the highly unsaturated liquid acids, by various methods. Pure clupanodonic acid could not be prepared by debromination of the bromides of the lower-boiling fractions of the ethyl esters. The most complete separation was obtained by reduction of the polybromides with zinc and methyl alcohol, followed by fractional distillation; the fraction b.p. 215° C. at 15 mm. (n_D^{20} 1·48060, iodine value 348·8) was probably pure methyl clupanodonate; the presence of several other acids was indicated by other fractions of methyl esters. Similar results were obtained with cod and herring oils.

The characteristics of Malabar sardine oil and its behaviour on refining, deodorising, hydrogenation, "splitting," and conversion into soap are described by J. J. Sudborough, H. E. Watson, and P. K. Kurup.⁴²

N. Evers and H. J. Foster⁴³ state that the delicacy of the sulphuric acid test for liver oils may be greatly increased by diluting the oil to be tested with an oil (e.g., olive oil) which itself gives no colour with sulphuric acid. H. D. Richmond and E. H. England⁴⁴ were unable to obtain good results with the sulphuric acid test as devised by Drummond and Watson⁴⁵ when petroleum spirit (recommended by the latter authors) was used instead of liquid paraffin. The addition of cholesterol, furfural, or ω -hydroxymethylfurfural to an oil dissolved in light petroleum was found by A. Harden and R. Robison⁴⁶ to cause the production of an intense purple colour with sulphuric acid, but no furfural or other substance yielding this reaction could be obtained by distillation or otherwise from coal-fish oil.

SOLID FATS.

Methods of differentiating genuine cacao butter from the many substitutes of cacao butter prepared from Borneo tallow, palm kernel and coconut stearines and other fats, or of detecting the addition of such substitutes of cacao butter have received a good

⁴⁰ *Chem. Umschau*, 1923, **30**, 33; *J.*, 1923, 276A.

⁴¹ *Ind. Eng. Chem.*, 1923, **45**, 1289; *J.*, 1923, 665A.

⁴² *J. Ind. Inst. Sci.*, 1923, **6**, 19; *J.*, 1923, 561A.

⁴³ *Analyst*, 1923, **48**, 58; *J.*, 1923, 275A.

⁴⁴ *Ibid.*, 1923, **47**, 431; *J.*, 1922, 902A.

⁴⁵ *J.*, 1922, 718A.

⁴⁶ *Biochem. J.*, 1923, **17**, 115; *J.*, 1923, 410A.

deal of attention, in the past, without, it must be confessed, any great measure of success.

According to M. Pichard⁴⁷ substitutes for cacao butter may readily be differentiated from genuine cacao butter, or their addition to cacao butter detected, by allowing the melted fat to cool in a suitable vessel and plotting the temperatures at intervals of five minutes; the cooling curves obtained with cacao butter differ widely from those obtained with the substitutes.

A method based on the curves obtained by observation of the miscibility with aniline-alcohol mixtures has been devised by Marange,⁴⁸ and is stated to enable the addition of 10% of other fats to cacao butter to be detected.

S. Kobayashi⁴⁹ has isolated a highly unsaturated hydrocarbon and higher alcohols from Indian illipé fat (*Bassia* species).

The characters of Indian mohua oil (*Bassia latifolia*) are described by J. J. Sudborough, H. E. Watson, and D. V. Chandorkar,⁵⁰ who have also investigated the behaviour of the oil on refining, hydrogenation, and "splitting." The choice of solvent for the extraction of fatty matter from oil-cakes etc. has always been one giving rise to some difficulty to the analyst; experiments by A. P. West and J. M. Feliciano⁵¹ on the extraction of copra cake with different solvents are distinctly interesting. Ether, carbon tetrachloride, or benzine was found to extract practically the same amount of "oil"; chloroform, acetone, and petroleum ether extracted a small amount of non-fatty matter in addition to oil. Much non-fatty matter was extracted by ethyl or methyl alcohol; the non-fatty matter extracted by methyl alcohol (after previous removal of oil with carbon tetrachloride) had high acid and saponification values and contained nitrogen probably present as amino-acid.

Comparatively little is known of the composition of the non fatty portion of even the most important commercial oil-seeds, and the authors' proposal to carry out further work is to be commended. The results also serve to emphasise the desirability—not recognised as widely as might be—of stating always the nature of the solvent used for determination of "oil" in oil-seeds and cakes.

The following glycerides were found by A. Bömer⁵² to be present in palm-kernel oil, caprylomyristolein m. p. 14°; dilauromyristin, m.p. 33°; laurodimyristin, m.p. 40°; dimyristopalmitin m.p. 45°; myristodipalmitin, m.p. 51°; caprylomyristolein constituted over 50% of the glycerides.

⁴⁷ *Comptes rend.*, 1923, **176**, 1224. *Ann. Faitsf.*, 1923, **16**, 197; *Analyse* 1923, **48**, 556; *J.*, 1923, 561A.

⁴⁸ *Ibid.*, 1923, **177**, 191; *J.*, 1923, 840A.

⁴⁹ *Kogyō-Kwagaku Zasshi*, 1922, **25**, 1188.

⁵⁰ *J. Ind. Inst. Sci.*, 1923, **6**, 133; *J.*, 1923, 562A.

⁵¹ *Philippine J. Sci.*, 1922, **20**, 509; *J.*, 1922, 866A.

⁵² *Chem. Umschau*, 1923, **30**, 202; *J.*, 1923, 1232A.

HARDENED OILS.

Although the hydrogenation of oils has been carried out on a very large scale for many years it is obvious from the amount and variety of research published recently that this field is by no means worked out.

The various forms of nickel catalysts used for hydrogenation and the factors influencing the activity of nickel catalysts are discussed in an interesting paper by R. Thomas.⁵³ Although this is not a very lengthy contribution it contains a great deal of valuable information in a comprehensive form, including a discussion on the various theories of hydrogenation and action of catalysts.

A short but interesting paper by T. P. Hilditch and C. W. Moore⁵⁴ on the selective hydrogenation of unsaturated glycerides includes the results of hydrogenation of maize, soya bean, linseed, and cotton-seed oils and of cotton-seed oil fatty acids, and also of the ethyl esters of the fatty acids, with nickel and in some cases copper catalysts. Several important facts are brought to light, such as the preferential hydrogenation of linolein and glycerides of less saturated fatty acids to olein before the olein is converted to stearin, but that this preferential hydrogenation is much less marked when the fatty acids are hydrogenated. The authors consider that selective hydrogenation is compatible with the Armstrong and Hilditch hypothesis of the formation of unstable intermediate compounds between catalyst and unsaturated compound, and that this hypothesis also explains the formation in the hydrogenation of ethyl oleate of ethyl claidate and of an ethyl iso-oleate with the double bond in a different position in the carbon chain.

The methods of producing an active surface on metallic nickel are discussed by E. J. Lush.⁵⁵ A catalyst of very high activity is produced by anodic oxidation of nickel turnings in an electrolyte,⁵⁶ followed by reduction in hydrogen. The catalyst produced in this way retains its activity for long periods when used for the continuous hydrogenation of oil. The results obtained on hydrogenating olive oil and cotton-seed oil by means of this catalyst in two different ways are interesting; when the catalyst is immersed in the oil and the oil allowed to overflow the hardened oil resembles that produced by means of powder catalysts and contains a similar amount of iso-oleic acid; if, on the other hand, a thin film of oil is allowed to drip over the catalyst, the hardened oil (of the same iodine value) contains a comparatively small amount of iso-oleic acid. The

⁵³ *J.*, 1923, 21T.

⁵⁴ *J.*, 1923, 15T.

⁵⁵ *J.*, 1923, 219T.

⁵⁶ E.P. 203,218; *J.*, 1922, 1080A.

power of easily controlling the formation of iso-oleic acid afforded by this process is, of course, of considerable technical importance.

The statements of previous observers⁵⁷ that the hydrogenation of oil may occur during hydrogenation are supported by W. Normann,⁵⁸ who suggests that dehydrogenation may account for the known difficulty of hydrogenation to an iodine value of 0 and for the formation of new unsaturated acids during hydrogenation owing to the addition of hydrogen atoms to one part and splitting off at another part of the molecule.

Dehydrogenation is stated by A. Brochet⁵⁹ to occur when hydrogenated castor oil is heated with a nickel catalyst at temperatures above 150° C., evolution of hydrogen being most rapid at 270°–280°. The dehydrogenated product, which differs from castor oil, is semi-solid (m.p. 74°, iodine value 20).

The influence of alumina and other oxides on the activity of nickel catalysts has been investigated by E. F. Armstrong and T. P. Hilditch,⁶⁰ who found that co-precipitation of the oxides of aluminium, iron (ferric), magnesium, or silicon up to about 2% increased the activity of nickel catalysts, but that larger amounts reduced activity. Increase of surface is regarded as the chief reason for increased activity.

Somewhat similar results are recorded by G. Kita and T. Mazume,⁶¹ who have studied the effect of the addition to nickel catalysts of from 2 to 16% of alumina, magnesia, calcium borate, calcium and magnesium phosphates, sodium carbonate, stearic and palmitic acids. Additions made to the catalyst before reduction generally increased activity, but sodium carbonate in any proportion was injurious; water is stated to have no injurious effect on nickel catalysts.

SOAPs.

Although the manufacture of soap has been carried on for many years past on an enormous scale it has been to some extent an empirical art rather than a branch of technology entirely controlled by science. The recent paper by K. MacLennan⁶² on the microscopic structure of soap is a most valuable contribution to the technology of soap manufacture; the author has examined microscopically soaps of individual fatty acids, and also commercial soaps, by means of polarised light, and describes and discusses the effects produced by different stages of manufacture, such as saponification, graining, fitting and finishing, setting and maturing.

⁵⁷ *E.g.*, *J.*, 1921, 397A.

⁵⁸ *Chem. Umschau*, 1923, **30**, 3; *J.*, 1923, 149A.

⁵⁹ *Comptes rend.*, 1923, **176**, 513; *J.*, 1923, 317A. *Bull. Soc. Chint.*, 1923, **33**, 626; *J.*, 1923, 787A.

⁶⁰ *Proc. Roy. Soc.*, 1923, **A103**, 586; *J.*, 1923, 786A.

⁶¹ *Rikwagaku Kenkyujo Ihō*, 1923, **2**, 1; *J.*, 1923, 728A.

⁶² *J.*, 1923, 393T.

Recently much attention has been given to the colloidal and physical properties of soap and soap solutions, and results of considerable scientific interest and technical importance have been obtained, both in this country and elsewhere, by the application of modern physico-chemical methods and views to various problems connected with soap.

A method of comparing the detergent power of soaps has been devised by J. W. McBain, R. S. Harborne, and A. M. King,⁶³ based on the determination of the amounts of colloidal carbon passing through a filter paper of a particular kind when carbon black is treated with soap solution under rigidly controlled conditions. A reliable test for the comparison of the detergent power of soaps is certainly much wanted, and it remains to be seen if the above test will furnish concordant results in the hands of different workers and will really give a true indication of the detergent value of a soap for any particular purpose.

The use of sodium silicates in soap has been perhaps a somewhat vexed question in the past; it has been discussed by A. S. Richardson⁶⁴ and also by W. Stericker.⁶⁵ The latter author considers the use of silicate is justified on account of its effect on the lathering and emulsifying properties of the soap.

For reasons of space it is scarcely possible to deal particularly with the numerous interesting papers on the physico-chemical and colloidal properties of soap solutions, but mention must be made of the following:—"Ultrafiltration of soap solutions; sodium oleate and potassium laurate" (J. W. McBain and W. J. Jenkins)⁶⁶; "Colloidal properties of soap solutions" (W. Prosch)⁶⁷; "Transition from colloidal to crystalloidal state; solutions of sodium oleate" (L. L. Bircumshaw)⁶⁸; "Surface properties of soap solutions" (J. F. Carrière)⁶⁹; "Soap solutions: sodium oleate and palmitate" (W. Leeten)⁷⁰; "Surface tension of alkaline soap solutions" (E. B. Millard)⁷¹; "Behaviour of soap solutions at various hydrogen ion concentrations" (A. Jarisch)⁷²; "Properties of sodium salts of fatty acids of medium molecular weights" (C. F. M. von Blamencron).⁷³

A comprehensive study of the oleates, stearates, and palmitates

⁶³ *J.*, 1923, 373T.

⁶⁴ *Ind. Eng. Chem.*, 1923, **15**, 241; *J.*, 1923, 364A.

⁶⁵ *Ibid.*, 244; *J.*, 1923, 364A.

⁶⁶ *Chem. Soc. Trans.*, 1922, **121**, 2325; *J.*, 1923, 104A.

⁶⁷ *Z. Deuts. Oel- u. Fettind.*, 1922, **42**, 410, 425, 433, 449, 462; *J.*, 1923, 104A.

⁶⁸ *Chem. Soc. Trans.*, 1923, **123**, 91; *J.*, 1923, 234A.

⁶⁹ *Chem. Weekblad*, 1923, **20**, 206; *J.*, 1923, 563A.

⁷⁰ *Z. Deuts. Oel- u. Fettind.*, 1923, **43**, 50, 65, 81; *J.*, 1923, 665A.

⁷¹ *Ind. Eng. Chem.*, 1923, **15**, 810; *J.*, 1923, 938A.

⁷² *Biochem. Zeits.*, 1922, **184**, 163; *J.*, 1923, 317A.

⁷³ *Z. Deuts. Oel- u. Fettind.*, 1922, **42**, 101, 130, 155, 171; *J.*, 1923, 150A.

of all the common metals has been made by H. J. Jones.⁷⁴ When dry, metallic soaps are mostly insoluble in water, alcohol, petroleum spirit and chloroform, but colloidal solutions are formed by the wet freshly prepared soaps. In many cases the technical value of the metallic soaps is dependent on retention of the colloidal state and certain waxes are good stabilising agents. The metallic soaps find application as driers in paints, in laundering and dry cleaning, in ointments and for waterproofing fabrics; in the latter use they act by reason of their colloidal state, adsorbing water and so filling up the pores of the material.

FATTY ACIDS.

The interest in the possibility of converting hydrocarbons into fatty acids referred to in last year's Report appears to be sustained, judging from the frequent patents referring to this subject, though it does not appear that production of fatty acids on a commercial scale has yet been attained. The problem is briefly discussed by R. Furness.⁷⁵

A useful contribution to the important technical question of the saponification of fatty oils has been made by H. M. Langton,⁷⁶ the author discussing the various theories of saponification and recording results of investigations on the splitting of tallow, palm, palm-kernel, linseed, and whale oils on a works scale. Apart from the author's own results, which are of interest, the paper contains numerous references to the work of previous investigators, which form a most useful bibliography on this subject.

The splitting of oils by castor seed lipase has been investigated by J. J. Sudborough and H. E. Watson,⁷⁷ who have carried out work with various Indian oils, and describe simple methods of making active lipase preparations.

The fractional distillation at low pressure of the methyl esters of fatty acids is a well-known and frequently used method of separating mixtures of fatty acids. E. Andre⁷⁸ finds that the separation of pure methyl linolate from a mixture of methyl oleate and linolate is difficult owing to polymerisation; the highest iodine value obtained for methyl linolate separated in this way was 160 (cf. pure methyl linolate 170.7).

The various recorded methods for the separation of liquid from solid fatty acids have been investigated by W. Meigen and A. Neuberger,⁷⁹ who found that quantitative separations were not

⁷⁴ *Chem. and Met. Eng.*, 1923, 28, 489; *J.*, 1923, 410A.

⁷⁵ *Chem. and Ind.*, 1923, 358.

⁷⁶ *J.*, 1923, 51T.

⁷⁷ *J. Ind. Inst. Sci.*, 1922, 5, 119; *J.*, 1923, 276A.

⁷⁸ *Comptes rend.*, 1923, 176, 686; *J.*, 1923, 364A.

⁷⁹ *Chem. Umschau*, 1922, 29, 337; *J.*, 1922, 944A.

attainable in any case. Precipitation of an aqueous solution of the potassium salts with thallous sulphate resulted in almost quantitative separation of palmitic, stearic, and claidic acids from oleic acid.

The structure of the molecule in the various fatty acids is a matter of the highest importance and scientific interest. The application of the X-ray spectrograph to this problem seems likely to produce most valuable results. A. Müller⁸⁰ has investigated several of the more common fatty acids and obtained results in accord with Friedel's theory. This work on the application of X-ray spectra to the examination of fatty acids has been summarised in a recent communication to the Journal.⁸¹

An unsaturated acid, linderic acid, $C_{12}H_{22}O_2$, isolated from the oil of *Lindera obtusifolia* B.L., has been examined and characterised by Y. Iwamoto.⁸²

R. Ehrenstein and H. Stuewer⁸³ find that isobehenic acid (isodocosanic acid, $C_{21}H_{43}COOH$) produced by degradation of lignoceric acid, is identical with arachidic acid from ground-nut oil, and that the fatty acid of m.p. 76°–77° C. from the oil of *Nephelium Lappaceum* is *n*-eicosanic acid, which is also obtained by fusion of erucic acid with potash.

Among the acids produced by electro-synthesis of an aqueous solution of potassium suberate and malonate, *n*-heptanedicarboxylic acid, identical with azelaic acid (produced from castor oil), has been identified by M. Carmichael.⁸⁴

The methyl, ethyl, acetyl, and benzoyl derivatives of hydroxystearic acid, produced by the action of sulphuric acid on oleic acid, have been prepared and characterised by L. G. Radcliffe and W. Gibson.⁸⁵

VARIOUS LESS KNOWN OILS.

It would scarcely be possible to refer in detail to all the recent investigations on less known oil-seeds and oils. Kaffir melon ("Tsamma") oil from the Kalahari region has been examined by C. F. Juritz⁸⁶; Brazilian "Coquilho" (*Attalea funifera*) nuts and oil by H. A. Gardner⁸⁷; seeds and oil of *Hibiscus cannabinus* by J. Dekker⁸⁸; oils from the kernel and arillus of seeds of *Afzelia africana* by A. Diedrichs and B. Schmittman⁸⁹; the pericarp and

⁸⁰ *Chem. Soc. Trans.*, 1923, **123**, 2043; *J.*, 1923, 987A.

⁸¹ *Chem. and Ind.*, 1923, 1099.

⁸² *Kogyō-Kwagaku Zasshi*, 1923, **26**, 708; *J.*, 1923, 786A.

⁸³ *J. prakt. Chem.*, 1923, **105**, 199; *J.*, 1923, 1031A.

⁸⁴ *Chem. Soc. Trans.*, 1922, **121**, 2545; *J.*, 1923, 104A.

⁸⁵ *J. Soc. Dyers and Col.*, 1923, **39**, 4; *J.*, 1923, 150A.

⁸⁶ *S. Afr. J. Ind.*, 1923, **6**, 67; *J.*, 1923, 317A.

⁸⁷ *Circ. 181 U.S. Paint Mfrs. Assoc.*, 1923; *J.*, 1923, 728A.

⁸⁸ *Pharm. Weekblad*, 1922, **59**, 1296; *J.*, 1923, 22A.

⁸⁹ *Z. Unters. Nahr. Genussm.*, 1922, **44**, 215; *J.*, 1923, 67A.

kernel oils of a species of *Sterculia* by C. D. V. George⁹⁰; oil of *Canarium opalum* by A. P. West and S. Balco.⁹¹

M. G. Rau and J. L. Simonsen⁹² have examined the oils (and identified the fatty acids present) of the following:—*Chloroxylon Swietenia*, *Calophyllum Wightianum*, *Mimosa Elengi*, *Shorea robusta*, *Garcinia Cambogiana*.

The following investigations of J. J. Sudborough and his co-workers on Indian oils (generally including the analytical character of the oils, the composition of the fatty acids, and information relating to the behaviour of the oils on refining, hydrogenation, and "splitting" by lipase) should also be mentioned. "Hongay" oil, from *Pongamia glabra*, by R. D. Desai, J. J. Sudborough, and H. E. Watson⁹³; oils of *Anacardium occidentale* ("Cashew") by C. K. Patel, J. J. Sudborough, and H. E. Watson⁹⁴; oils of *Calophyllum Wightianum* and *Hydnocarpus Wightiana* by I. Joseph and J. J. Sudborough⁹⁵; "Mohua" oil (from *Bassia latifolia*) by J. J. Sudborough, H. E. Watson, and D. V. Chandorkar.⁹⁶

METHODS OF ANALYSIS AND TESTING.

The mathematical relationships existing between the different analytical "constants" of many representative fats and fatty acids are fully discussed in an interesting paper by J. Lund.⁹⁷ An exhaustive comparison of Aschman's method of determining the iodine value of oils, in which use is made of aqueous iodine monochloride solution, with other methods has been made by B. M. Margosches, R. Baru, and L. Wolf.⁹⁸ As it is necessary to allow the mixture to stand for at least 24 hours, or for 6 hours with shaking if the oil is dissolved in a solvent, it hardly seems that this method will find favour when rapid and accurate methods—such as that of Wijs—are already so largely used.

The endeavour made by D. W. Steuart to work out a method of analysis of fat mixtures of margarines by determination of the sterol content of the unsaponifiable matter unfortunately did not lead to success, though his paper contains a good deal of information of interest with regard to unsaponifiable matter in the various edible oils.⁹⁹

⁹⁰ *Malay Agric. J.*, 1922, **10**, 284; *J.*, 1923, 462A.

⁹¹ *Philippine J. Sci.*, 1923, **23**, 269; *J.*, 1923, 1079A.

⁹² *Ind. Forest Rec.*, 1922, **9**, Pt. III.; *J.*, 1922, 902A.

⁹³ *J. Ind. Inst. Sci.*, 1923, **6**, 93; *J.*, 1923, 987A.

⁹⁴ *Ibid.*, 1923, **6**, 111; *J.*, 1923, 987A.

⁹⁵ *Ibid.*, 1923, **5**, 133; *J.*, 1923, 562A.

⁹⁶ *Ibid.*, 1923, **6**, 1; *J.*, 1923, 562A.

⁹⁷ *Z. Untere. Nahr. Genussm.*, 1922, **44**, 113; *J.*, 1922, 944A. *Chem. Umschau*, 1923, **30**, 74; *J.*, 1923, 410A.

⁹⁸ *Z. anal. Chem.*, 1923, **62**, 178; *J.*, 1923, 304A.

⁹⁹ *Analyst*, 1923, **48**, 155; *J.*, 1923, 462A.

The various factors influencing the determination of viscosity by means of the Redwood viscometer are discussed by W. H. Herschel.¹⁰⁰ Factors for comparison of Redwood, Saybolt, and Engler viscosities are given. In view of the fact that rape oil has been used as a "standard" oil for viscosity work it is of interest to note that this oil was found to vary in viscosity by 27%.

The work of G. T. Bray and F. Major on the determination of fat in casein¹⁰¹ should serve to show once and for all that fat cannot be extracted quantitatively by solvents from casein powder. These authors obtained good results by the Werner-Schmidt method and somewhat low results by the Röse-Gottlieb method.

WAXES.

The wax coating the stems of Australian "cane" or "bamboo-grass" (*Glyceria ramigera*) has been investigated by H. G. Smith.¹⁰² In appearance, hardness, and melting point this wax is similar to carnauba wax.

Ceryl cerotate occurs in the husks of sunflower seeds, and has been obtained by A. Bareuther¹⁰³ from the deposit at the bottom of tanks in which sunflower seed oil was stored.

¹⁰⁰ U.S. Bureau of Standards, *Tech. Paper* 210, 1922, 227; *J.*, 1923, 77A.

¹⁰¹ *J.*, 1923, 106T.

¹⁰² *J.*, 1923, 372T.

¹⁰³ *Chem. Umschau*, 1923, 30, 117; *J.*, 1923, 612A.



PAINTS, PIGMENTS, VARNISHES, AND RESINS.

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THE literature of the paint and varnish industry shows a steady annual increase, which is indicative of greater interest in the subject and of appreciation of its importance. The efforts of the U.S. Paint Manufacturers' Association have stimulated the investigation of the many problems of the industry. The tendency towards standardisation in the United States encourages co-ordination of physical and chemical properties with the requirements of practice. It is true that many of the specifications under which materials may be bought are inadequate and require constant revision. For the raw materials of the industry, e.g., oils, pigments, and a few resins, success of standardisation is more assured, but when applied to the finished products of the industry correlation of physical and chemical properties with trade requirements becomes difficult. The spirit of standardisation is spreading to this country in a more restrained form, being restricted to the requirements of Government Departments, which demand compliance with specifications. Many of these specifications are accepted by manufacturers with due regard to their limitations, but in the case of finished products the requirements are so many and so varied that it would be difficult to lay down hard and fast rules governing quality. In the section of this Report dealing with varnishes, it will be shown how difficult it is to guarantee the durability of films, when so much depends on the quality of the undercoats and on the conditions of application.

In the survey of the year's work special reference has been made to the sources of the raw material, the supply of which influences so largely the development of production. There is a tendency to explore for new drying oils which will give greater durability and better lustre than are obtained with linseed oil. The Royal Academy has formed a Committee of artists and scientists to investigate the qualities of artists' materials and the various methods of cleaning pictures. It is possible that the peculiar property of the yellowing of linseed oil films and the permanence of pigment colours will receive further attention. The importance of the study of the chemical composition of the resins has not been

neglected, especially the composition and properties of the components of resins from their many sources. The colloid characters are being carefully considered in accounting for differences in properties, which are difficult to explain and where the influence of chemical composition appears to fail. The literature on synthetic resins is voluminous and their uses are becoming more popular with the discovery of special new properties. The Report of the Home Office Committee on the use of lead pigments has broadened the outlook on the difficulties of the situation and has probably made it easier to construct a policy for dealing with the problem. The work of Bingham and Green on the properties of plastic flow has raised criticisms on some of the results, but the value of their investigations becomes more and more recognised by all students of paints. In the varnish section the necessity for improvement of analytical methods is great, especially when small samples have to be examined. A new method for the separation of drying oils and resins is required, with satisfactory identification of the separated components of varnishes. Unanimity is desired for deciding standard durability tests, especially where organic coatings are employed in the protection of metals.

DRYING OILS.

In an interesting survey of the world's production of flax seed and linseed oil¹ it is shown that during the past four or five years Argentina has produced more than half the world's output of linseed. Prior to 1916 Russia was one of the largest producers of flax seed, but since that year Argentina, British India, the United States, and Canada have produced 90% of the total supply. Although the acreage of the Argentine crop is 1% above the pre-war acreage average, yet the crop for 1922 is estimated to be 50% greater. In British India (the second largest producer) the average acreage is 20% less than the average pre-war area, whilst the supply is dependent on weather conditions. In the United States and in Canada the decline is more marked, due partly to the competition of wheat, which is more profitable. The United States, Great Britain, France, Belgium, Italy, the Netherlands, and Germany crush more than 95% of all flax seed entering into national commerce. Prior to the war Germany was the largest net importer of flax seed, but in 1922 the supply had reverted to one-third of the pre-war volume. It is estimated that the consumption of linseed oil in 1922 in Europe is probably 40 million gallons less than pre-war, but decreased consumption in Europe is counterbalanced by increased consumption in the United States, which imported 19 million gallons in 1922.

¹ *Commerce Monthly*, New York, June, 1923.

Already steps are being taken in the last-named country to prevent the decline of home production.

The maintenance of the immediate demand for linseed oil will depend in a large measure on widespread continuance of building activity, and the permanent maintenance of consumption requirements at a relatively high level seems probable. An interesting review of the linseed oil industry has appeared,² in which the future prospects of the linseed industry are discussed. The number of contributions on the drying of linseed oil during 1923 is very limited and the results are not striking. H. A. Gardner and H. C. Parks³ have examined the influence of coloured and ultra-violet light on the drying of linseed oil. As would be expected, the screening of ultra-violet rays by red glass showed a loss of accelerating effect. F. H. Rhodes and A. E. van Wirt⁴ have investigated the effects of various pigments upon the rate of oxidation of linseed oil. Their conclusions are that the drying of linseed oil is an autocatalytic reaction. The real catalyst is the oil itself, and the effect of lead salts in accelerating the drying of the oil is due to the fact that these salts are pseudocatalysts, promoting the formation of the autocatalysts and thus increasing the rate of oxidation when the oil is first exposed to air. It is considered by most workers that the drier takes the place of the autocatalyst. The lead drier is stated to have no marked effect on the total amount of oxygen ultimately absorbed by the oil.⁵ The influence of pigments is:—(1) passive, as in the case of silex; (2) reducing the rate of oxidation, quantity of oxygen absorbed, and volatile matter liberated as in the case of lithopone, titanium dioxide, and barium sulphate pigments; (3) increasing the amount of oxygen absorbed, when white lead and basic lead sulphate are used. Zinc oxide acts as belonging to class (1) or (2). The authors state that the results are preliminary.

From the examination of several hundred samples of commercial linseed oil, H. Wolff⁶ has given the average limiting values of the analytical characteristics, and states that I.V. (Hübl)=I.V. (Wijs)
—[I.V.(Wijs)-140]×0.2 holds for linseed oil.

The same author⁷ examines the oil obtained from paints by determination of its refractive index, which is normally 1.480–1.486. A higher refractive index shows the presence of resins, which are separated from the oil by the method of Wolff and Scholze.⁸ The investigation of H. Wolff and C. Dorn⁹ on the nature of deposits in

¹ *Chem. Trade J.*, Nov. 11, 1923.

² H. A. Gardner and H. C. Parks, *Circ. 172, U.S. Paint Manuf. Assoc.*, 1923; *J.*, 1923, 463A, and *J.*, 1919, 915A.

³ *Ind. Eng. Chem.*, 1923, 15, 1135; *J.*, 1923, 1233A.

⁴ Cf. S. Coffey, *Chem. Soc. Trans.*, 1922, 121, 17.

⁵ *Chem.-Zeit.*, 1923, 47, 142; *J.*, 1923, 275A.

⁶ *Farben-Zeit.*, 1923, 28, 931; *J.*, 1923, 411A.

⁷ *J.*, 1914, 363.

⁸ *Oil and Colour Tr. J.*, 1923, 1002.

boiled oils and varnishes discloses the already well-known fact of the presence of lead palmitate and stearate and that demucilaginated oils have a greater tendency to form separations than mucilaginous oils. Nevertheless they do not refer to methods of dealing with gum-oil complexes in varnishes, which persist after the lead salts of the saturated acids have been deposited. E. André¹⁰ has found that it is impossible to effect a complete separation of methyl linolate from methyl oleate by distillation *in vacuo* (2–3 mm.) owing to the polymerisation of the former ester on continued heating. In view of the possible use of anhydrides of unsaturated acids the preparation and properties of the anhydride of linolic acid are of interest.¹¹ R. J. Anderson and M. G. Moore¹² conclude that linseed oil contains at least two phytosterols, which differ in melting points and optical rotations, but it must be confessed that the differences are not very marked. Cottonseed oil is also stated to contain more than one phytosterol.

H. A. Gardner and P. C. Holdt¹³ recommend specifications for aluminium stearate, which is used to give body to and to prevent settling in ready mixed paints, as well as to confer water-resisting properties on washable distempers and to give an egg-shell gloss finish to furniture varnishes. There are two papers which were omitted in last year's Annual Report and are worthy of reference. D. Holde and collaborators¹⁴ recommend the use of Hanus' reagent in the determination of the iodine value of the higher aliphatic and aromatic unsaturated compounds.¹⁵ The peculiar property of glycerides in possessing a double melting point has led A. Grün¹⁶ to propose two formulæ, R.CO.OR and RC $\begin{array}{l} \diagdown \\ O \\ \diagup \end{array}$ R to account thereby for their unusual reactivity, which frequently resembles that of salts, except in greater slowness of reaction. This proposal is of interest in connexion with the different behaviour of the glycerides of drying oils compared with the methyl and ethyl esters.

H. A. Gardner¹⁷ has patented a process for the chlorination and dechlorination by a catalyst of non-drying and semi-drying oils to produce drying oils, which are viscous, and still retain 40–60% of the chlorine introduced.¹⁸ The Badische Anilin und Soda-Fabrik¹⁹ claim the production of drying oils from petroleum and tar oils

¹⁰ *Comptes rend.*, 1923, **176**, 686; *J.*, 1923, 304A.

¹¹ D. Holde and S. Weill, *Chem. Umschau*, 1923, **30**, 198, 205; *J.*, 1923, 896A, 938A.

¹² *J. Amer. Chem. Soc.*, 1923, **45**, 1953; *J.*, 1923, 937A.

¹³ *Paint Manuf. Assoc., U.S.A.*, *Circ.* 182, 1923; *J.*, 1923, 730A.

¹⁴ *Chem. Umschau*, 1922, **29**, 185; *J.*, 1922, 557A.

¹⁵ Maclean and Thomas, *Biochem. J.*, 1921, **15**, 319.

¹⁶ *Oesterr. Chem.-Zeit.*, 1922, **25**, 37; *J.*, 1922, 334A.

¹⁷ U.S.P. 1,452,553; *J.*, 1923, 667A.

¹⁸ U.S.P. 1,463,884; *J.*, 1923, 1032A.

¹⁹ G.P. 379,530; *J.*, 1923, 1186A.

using phosgene. The specifications for China wood oil drawn up by the A.S.T.M. are acceptable to importers and consumers, with the exception of the heat test. The modified Browne test should be supplemented by that of Worstell, in which the character of the solid polymerised gel and its colour can be observed.²⁰

Further investigations on the properties of wood oil have not contributed much to the knowledge of the subject, and papers by J. Marcusson and by F. H. Rhodes and T. J. Potts contain much that was previously known. Marcusson²¹ has examined the formation of the solid modification of β -elæostearin and has confirmed earlier published work on the subject, but the statement that the action of air or light on the solid modification produces polymerisation requires confirmation, because the white crystalline substance is very oxidisable. Similarly the formula of elæostearic acid given by A. Vereruyse²² is the same as that given originally by Majima. Vereruyse found that on oxidation by potassium permanganate elæomargaric acid gave an amount of carbon dioxide corresponding with four atoms of carbon in the molecule, in addition to azelaic and valeric acids. The detection of succinic acid in the presence of azelaic and valeric acids had been unsuccessful.²³ F. H. Rhodes and T. J. Potts²⁴ in their investigation of the inhibition of the gelation of tung oil state that the efficiency of glycerol, oleic acid, rosin, ester gum, paracoumarone resin, and linseed oil are in the order given. It must be pointed out that the retardation of gelatinisation of tung oil by glycerin at 280° C. requires the retention of glycerin in the system, otherwise the retardation is very slight. The presence of free glycerin in wood oil mixings is detrimental to the quality of the films. F. H. Rhodes and H. E. Goldsmith²⁵ have determined the variation in the refractive index of China wood oil with temperature and fix it at 0.0004 per 1° C. C. F. Mabery²⁶ also contributes to the discussion on the heat treatment of tung oil.

Among the investigations on other drying oils mention may be made of papers by C. T. Wang,²⁷ who advocates the revival of the perilla oil industry in China, and considers that its drying qualities are superior to those of tung oil, which has so largely superseded it. K. H. Bauer²⁸ and R. Hardegg²⁹ independently have examined perilla oil by the usual methods employed in the investigation of drying oils. The acids identified were palmitic, oleic (5.7%),

²⁰ E. W. Fasig, *Chem. Abstracts*, 1923, 640.

²¹ *Z. Deuts. Oel- u. Fett-Ind.*, 1923, 43, 102; *J.*, 1923, 938A.

²² *Bull. Soc. Chim. Belg.*, 1923, 32, 151; *J.*, 1923, 665A.

²³ *Chem. Soc. Trans.*, 1912, 101, 2089.

²⁴ *Chem. and Met Eng.*, 1923, 29, 533; *J.*, 1923, 1031A.

²⁵ *Ind. Eng. Chem.*, 1923, 15, 786; *J.*, 938A.

²⁶ *Ibid.*, 1923, 15, 365; *J.*, 1923, 563A.

²⁷ *J. China Soc. Chem. Ind.*, 1923, 1, 11.

²⁸ *Chem. Umschau*, 1923, 30, 9; *J.*, 1923, 149A.

²⁹ *Ibid.*, 1922, 29, 301.

linolic, and linolenic acids. The oxidation products from the potassium permanganate treatment, when extracted by the Heiduschka method, gave a mixture of mono-, di-, tetra-, and hexa-(normal and iso-) hydroxystearic acids. The authors admit that the oxidation method employed is not ideal for quantitative work.

The marketable supply of oitica (oticica) oil does not appear available, although the oil would be of value for both the paint and varnish trades.³⁰ An interesting summary of the fish oil industry is given in (1) an article by P. T. Bruyère,³¹ comprising the refining, bleaching, blowing, and utilisation of the foots of the oil, and (2) a communication entitled "The technology of fish oils."³² Fish oils are now largely used, especially in America, in combination with linseed oil and also as a direct substitute for it. The fish oils are said to be more heat-resisting, so that they may be used on iron work exposed to relatively high temperature and generally for work in which their quick drying and binding qualities are valuable. The chemistry of menhaden oil and other fish oils is by no means clear. M. Tsujimoto³³ ascribes the formula ($C_{22}H_{34}O_2$) to clupanodonic acid, which he obtained from Japanese sardine oil by the polybromide method and the lithium salt acetone method.³⁴ J. B. Brown and G. D. Beal,³⁵ from observations on the methyl esters obtained from menhaden oil, conclude that in addition to clupanodonic acid ($C_{18}H_{28}O_2$), there are present hexadecatrienoic ($C_{16}H_{26}O_2$), linolenic, arachidonic ($C_{20}H_{32}O_2$) (4), eicosapentenoic ($C_{20}H_{36}O_2$) (5), docosapentenoic ($C_{22}H_{34}O_2$) (6), and docosahexapioic ($C_{22}H_{32}O_2$) (7) acids as well as myristic, palmitic, and palmitoleic acids. The figures in brackets indicate the number of double bonds presumed to be present in the molecule of the acids. Careful fractional distillation of the methyl esters indicated the presence of C_{14} , C_{16} , C_{18} , C_{20} , and C_{22} acids and one fraction is practically pure methyl clupanodonate. It would appear as if some new reagent or some new reaction were required to effect the separation of the unsaturated acids of drying oils. W. Meigen and A. Neuberger,³⁶ in the examination of the quantitative methods for the separation of solid and liquid fatty acids, consider that the methods of Bull, Fjellanger, Fachini and Dorta, and David yield approximately half of the liquid acids in a pure condition. They state that a quantitative separation to 96% of oleic acid from stearic acid can be effected by their thallium salts.

³⁰ H. A. Gardner, *Paint Manuf. Assoc., U.S.A.*, Circ. 177, 1923.

³¹ *Oil, Paint and Drug Rep.*, 1923.

³² *Chem. Trade J.*, 1922, 655.

³³ *J. Chem. Ind. Japan*, 1923, 26, 1013; *J.*, 1923, 1185A.

³⁴ *J.*, 1920, 825A.

³⁵ *J. Amer. Chem. Soc.*, 1923, 45, 1289; *J.*, 1923, 665A.

³⁶ *Chem. Umechau*, 1922, 29, 337; *J.*, 1922, 944A.

A. Eibner³⁸ maintains that the yellowing of linseed oil films is a particular effect of free linolenic acid (produced by aqueous hydrolysis) or its peroxide. It is noticeable that the yellowing effect is not apparent when poppy or nut oil films are subjected to the same conditions.

The crystalline bromides of linseed oil have been investigated by H. Toms,³⁹ who states that they consist of mixtures of (1), linolic-dilinolenic bromoglyceride, m.p. 153°C., and (2) trilinolic bromoglyceride or oleic-linolic-linolenic bromoglyceride, m.p. 177°, in varying proportions. The bromoglycerides have been obtained pure by crystallisation from ethyl acetate. It is probable that the uncertainty of determination of linseed oil by means of its bromo-derivatives is due to the formation of the above mixtures.* Analyses of chia, rubber seed, sunflower, and tung oils are contained in a report of the Society for Testing Materials.⁴⁰ It is recommended that the treatment of tung oil with lime should be omitted before applying the heat test.

RESINS.

It is often difficult for the student to find statistics of the production of raw materials required in an industry, especially in that connected with the manufacture of paints and varnishes. During the year three papers have been published, recording the production of turpentine and rosin in America, France, and Russia. The United States provide 60–65% of the world's supply of turpentine and 70% of the rosin, of which 35–40% of the turpentine and 30% of the rosin are used in that country. England is the second great consumer of these materials. The distribution of turpentine in industry is as follows: paints and varnishes require 48%; paint and varnish thinners, 40%; polishes for boots, etc., 6%; pharmaceutical preparations, 2%, and other uses, 4%. The distribution of rosin in the various trades is: soap industry, 42%; paper industry, 25%; paints and varnishes, 17%; linoleum, 3%; rosin oil, pitch, and printing colours, 6%; other uses, 7%. The distribution in England is practically the same as in the United States. The export of turpentine from the United States was 9,864,000 gallons and 799,000 barrels of rosin, which is a reduction on the pre-war export. Wood rosin obtained by extraction from pine stumps is now offered from America.⁴¹ The output of turpentine and rosin in France has increased compared with pre-war figures. In 1913 25,000 metric tons of turpentine and 85,000 metric tons of rosin were produced. In 1922 the turpentine output had risen to

³⁸ *Bayer. Ind. Gewerbeblatt*, 1922, **64**, 105, 113, 117; *J.*, 1923, 190A.

³⁹ *Oil and Col. Tr. J.*, 1923, 2041.

⁴⁰ *Proc. Amer. Soc. Testing Materials*, 1922, **22**, I., 367.

⁴¹ *F. Goldschmidt, Oel- und Fettind.* 1923, **43**, 370.

32,000 metric tons and the rosin to 118,000 tons. France now produces one-sixth of the world's output and 28% of the turpentine with 50% of the rosin of the French crop are exported from the country.⁴² The temperature coefficient of the refractive index (n_D) of American turpentine is 0.000468.⁴³ An interesting summary of the production of Russian turpentine is given by B. Smirnoff.⁴⁴ At the present moment the All Russian Co-operative Union of Wood-Working and Wood-Converting Associations, "Vsekoless," has succeeded in uniting the majority of producers. According to the author of the paper, the system of specifications and trade marks to be adopted will remove all doubt as to the exact nature of any brand of Russian turpentine offered. The varieties are: virgin dip (from Archangel only); steam-produced (by the action of steam on stumps); retort-produced; boiler-produced and pitch turpentines. Each class has a number of varieties with a total of 21. For details the original paper must be consulted, in which will be found fractionation values, specific gravities, and colour grade of the varieties.

In continuance of the statistics of the production and sources of resins, reference may be made to the export of copal from the Congo region and a recent report on the kauri industry of New Zealand. The export of copal from the Congo to Antwerp in 1922 was 13,000 tons (35 million francs), but in 1923 a reduction is expected, because of the exhaustion of stocks in the Congo region.⁴⁵

A useful report on the kauri industry of New Zealand is to be found in the Bulletin of the Imperial Institute (1922, p. 331). The present-day aim is to recover all the gum that the land contains, even down to the finest particles. In the modern methods of obtaining the resin, the soil is puddled with water and sieved through various meshes, using mechanical agitators, or the swamp material after being mixed with water is raised by an elevator into a special disintegrator for breaking up the soil only, and the gum passes into cylindrical screens of diminishing mesh. The gum is purified by the Maclaurin process, which consists of treatment with a brine solution ($d\ 1.15$), in which the gum floats. The grading depends partly on colour and on the place of origin. The bleeding or tapping of the living tree (*Agathis australis*) is forbidden in the State forests. Of the exported kauri, 60%, usually of low grade, is used for linoleum. The total export in 1920-21 was 6131 tons, of which the United States took 3224 tons, valued at £345,992, and the United Kingdom 2554 tons, value £149,422. The Report of the Commission of 1921 recommends that there should be a standard

⁴² *Chim. et Ind.*, 1923, 428.

⁴³ G. Thompson, *Analyst*, 1922, 47, 469; *J.*, 1923, 62A.

⁴⁴ *Chem. Trade J.*, 1923, 600.

⁴⁵ *Chim. et Ind.*, 1923, 383.

grading for export, the methods of recovering gum from gum-bearing soils should be improved by the introduction of more efficient methods, by the use of washing plants and the application of the Maclaurin process. Further scientific investigations should be carried out on the effects of "bleeding" trees, on kauri peat, and on all the products of the kauri forests. When kauri peat is distilled 40 gallons per ton of peat is obtained, which on fractional distillation gives 10% of a motor spirit, 80% of heavier oils, and 10% of pitch. The black peat above the so-called kauri peat on distillation gives 20–30 gallons of oil per ton of peat.

A. H. Gill and D. Ni-hida⁴⁶ have contributed some notes on the oil from kauri copal. The observations are evidently of a preliminary character, but it is stated that the middle and higher fractions of the oil, unlike rosin oil, gave no retene.

In the investigation of the chemical composition of the natural resins further work on amyrin from manila resin has been carried out by A. Rollett and K. Bratke.⁴⁷ They have obtained from β -amyrin by oxidation with potassium persulphate crystalline hydroxy- β -amyrin acetate $C_{30}H_{47}O.CO.CH_3$, m.p. 291°–292° C.; also hydroxy- β -amyrin (cryst.) $C_{30}H_{47}O.OH$, m.p. 200°–201° C., which on oxidation by chromic acid yielded hydroxy- β -amyrone, $C_{30}H_{46}O_2$, m.p. 216°–217° C., which yields an oxime.

H. Jansch and P. Fantl⁴⁸ continuing the work of Wallach, Clover, Semmler and Liao, have examined the crystalline solid occurring in the elemicin fraction (b.p. 140°–150° at 10 mm.) of elemi oil and have shown it to be a bicyclic sesquiterpene alcohol (α -elemol $C_{15}H_{26}O$) with only one double bond. It is isomerised to β -elemol (monocyclic terpene alcohol) during benzoylation. On reduction by zinc dust α -elemol yields elemane, $C_{15}H_{26}$ (b.p. 115°–119° C.).

J. L. Simonsen⁴⁹ concludes from an examination of the essential oil of *Boswellia serrata* that *d*- α -pinene is not present, as stated by Pearson and Puran Singh in 1918, but that the essential oil consists of α -thujene (b.p. 152°–155° C. at 699 mm; $a^{20} = 37.69^\circ$; $n_D^{20} = 1.4502$). The same author⁵⁰ has investigated *d*-longifolene occurring in the higher boiling fractions of Indian turpentine. *d*-Longifolene is a sequiterpene, but not a naphthalene derivative. On oxidation it yields two isomeric longifolic acids ($C_{14}H_{22}O_3$). Further oxidation gives small quantities of α -dimethylsuccinic acid, and from the main bulk of the oxidation product a crystalline orthodiketone (*d*-longif-1,2-dione), $C_{15}H_{22}O_2$, was isolated.

A recently issued Bulletin (No. 142) of the Agricultural Research Institute, Pusa, by C. S. Misra, contains an account of the culti-

⁴⁶ *Ind. Eng. Chem.*, 1923, **15**, 1276; *Abs.*, 1924, **B**, 63.

⁴⁷ *Monatsh.*, 1923, **43**, 685; *J.*, 1923, 574A.

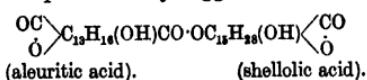
⁴⁸ *Ber.*, 1923, **56**, 1363; *J.*, 1923, 799A.

⁴⁹ *Indian Forest Records*, 1923, **9**, 289; *J.*, 1923, 627A.

⁵⁰ *Chem. Soc. Trans.*, 1923, **123**, 2642; *J.*, 1923, 1247A.

vation of the lac insect in the plains of India, including its life history and the manufacture of shellac and other phases of the subject. No outline can do full justice to the Bulletin, which all those who are interested in the subject should obtain for themselves.⁵¹ H. Vollmann⁵² gives a summary and review of the recent work of Harries and Nagel, Tschirch, Aschan and others on the constitution of shellac and of the conifer resins. The production of shellac and its decomposition products have been discussed by A. Tschirch.⁵³ The shellac resin and wax are considered to be built up by the lac insect and not absorbed ready made from the plant. The red colouring matter has its origin probably in the activity of red bacteria in the body of the insect, the resin being secreted from glands distributed over the whole surface of the insect, while the wax is secreted from localised glands. The chief products of successive extraction of stick-lac with water, alcohol, xylene, and caustic soda are laccaic acid ($C_{20}H_{14}O_{10}$); an acid resin containing an ether-insoluble volatile odoriferous crystalline substance, also golden-yellow erythrolaccin ($C_{15}H_{10}O_5$), soluble in ether, related to emodin, aleuritic acid, $C_{16}H_{22}O_5$ (insoluble in ether), wax, and a third dye-substance related to the laccaic acid located in the body of the insect.

C. Harries and W. Nagel⁵⁴ have continued their investigations on the nature of shellac and have isolated shellolic acid (shellene-dioildicarboxylic acid, $C_{15}H_{20}O_8$), which is an unsaturated di-hydroxy-carboxylic acid. They conclude that it is very improbable that shellac resin is the aleuritic ester of a higher alcohol, since no trace of the latter could be detected, and as the resin does not contain free acid, it appears probable that the shellac molecule is composed of hydroxy-acids united in the form of lactides. For one of the simpler components they suggest the following formula :—



the composition of which is closely similar to that of the pure resin.

P. H. Walker and L. L. Steele⁵⁵ have discussed the production of shellac and its grading and have drawn up specifications for orange shellac and orange shellac varnish. The paper is worthy of careful reading in view of the many inadequate specifications in use by purchasers of the resin. The commercial grading of shellac is based generally on freedom from rosin and dirt and on the colour of the resin flakes. The Liebermann-Storch reaction is sensitive to about

⁵¹ Oil and Col. Trades J., Sept. 15, 1923.

⁵² Farben-Zeit., 1923, 28, 486, 562.

⁵³ Chem. Umschau, 1922, 29, 349.

⁵⁴ Ber., 1922, 55, 3833; J., 1923, 105A.

⁵⁵ U.S. Bureau of Standards Tech. Paper, 232, 1923; J., 1923, 563A.

5% rosin content. Walker and Steele recommend the use of the Halphen-Hicks reagent for the detection of rosins, but it is doubtful as to whether it is superior to that of Liebermann and Storch. Wijs' method for the determination of the iodine value is now considered to be inapplicable to shellac solutions. The authors recommend McIlhiney's process⁵⁶ for the determination of the rosin content of shellac. For further details of the specifications the original paper may be consulted with advantage.

F. Simion⁵⁷ calls attention to the comparative neglect of the study of natural resins by scientific workers. Innumerable problems remain to be solved in connexion with the natural resins, and it may be prognosticated with certainty that every advance in the scientific knowledge of these materials will be directly accompanied by equally important developments in their technical application. When it has been determined which of the components of the natural resins are the cause of certain valuable properties (hardness, elasticity, resistance to chemical reagents, electrical insulating properties) and which act as a ballast or even retard the desired effect, it will then be possible not only to determine the value of a resin by analysis, but also to prepare lacquers and insulating materials of hitherto unknown excellence.⁵⁸ It will be some time before the expectations of Simion will be realised, but there is no doubt that further investigation of the resins will bring a valuable reward. The following investigations in the paper are worthy of mention: the results of two methods of the determination of the solubility of copals in alcohol are stated to give results with an error of only 0.5%. The changes in the copals on melting are of interest, and although the author states that the running of copals has not been scientifically investigated, yet there is much more known in the trade than the author imagines. Attempts to remove the dark colour of acaroid resin have not been successful. The red acaroid is bleached only temporarily, especially in acid solution by reduction and the solution soon acquires a red colour much more rapidly than in the case of a bleached solution of the yellow acaroid resin. C. H. Moulder and F. P. Gulley⁵⁹ describe a method of treatment of *Xanthorrhoea* gums for the production of dyes and stains.

In view of the restricted data as to the composition of resins, their classification and analysis can only be approximate. P. C. Holdt, H. A. Gardner, and P. E. Jameson⁶⁰ propose a classification by determination of the resin acids and unsaponifiable matter and of the solubility of these fractions. Group I contains resins completely soluble in alcohol and benzol (1 : 1), and consisting almost entirely

⁵⁶ J., 1908, 579.

⁵⁷ Chem.-Zeit., 1923, 47, 141; J., 1923, 278A.

⁵⁸ Oil and Col. Trades J., 1923, 818.

⁵⁹ E.P. 200, 942; J., 1923, 939A.

⁶⁰ Paint Manuf. Assoc., U.S.A., Circ. 159, 1923; J., 1923, 22A.

of saponifiable free resin acids with small amounts of volatile and unsaponifiable matter. To this group belong kauri, manila, pontianak, Borneo, and the live conifer resins (rosin and sandarach). Group 2 contains Zanzibar, Mozambique, Madagascar, Brazil, Congo, Sierra Leone, Angola, Benguela, Accra and other West African copals, consisting of saponifiable resin acids (soluble in alcohol-benzol) and an unsaponifiable portion insoluble in any known solvent. Group 3 contains East Indian copal and black dammar with an unsaponifiable portion soluble in benzol, insoluble in alcohol, and containing a relatively smaller amount of saponifiable matter. Groups 1 and 2 are further divided into sub-groups, characterised by different limiting values. With certain resins considerable differences were found between the direct and indirect acid values; this is usually designated as the ester value, but the authors believe that the differences are due to aldehydes and call them aldehyde numbers. The Circular contains a complete bibliography on varnish resins.

An investigation on the components of two forms of amber, succinite and gedanite, has been carried out by A. Tschirch, E. Aweng, C. de Jong, and E. S. Hermann.⁶¹ They find the two forms are alike in regard to chemical composition. The method of separation of the component acids is on the usual lines, and the alcohol-insoluble portions of the resins when hydrolysed with alkali give succinic acid (2%), and succino-resinol (3%) $C_{12}H_{20}O$, leaving a residuo of succino-rosene, $C_{22}H_{36}O_2$, m.p. $324^\circ C.$, which is 65% of the original amber. The resene is indifferent to alkalies and insoluble in solvents except aniline, pyridine, and phenol. Amber differs markedly from recent conifer resins in this high proportion of the resene. The possibility of the formation of a resene from rosin is an interesting speculation.

Among the communications on colophony Schorger⁶² has adduced evidence to show that the crystallisation of rosin is not due to hydration,⁶³ and that rosin does not consist of abietic anhydride.⁶⁴ O. Aschan and H. Karstrom⁶⁵ state that the specific rotation [α_D^{20}] of some colophony acids varies between $+5^\circ$ and $+67^\circ$ in benzene (in alcohol the variation is less), but a specimen obtained from Finnish varieties was strongly laevorotatory. F. P. Veitch and W. F. Sterling⁶⁶ point out the importance of considering the changes in powdered rosin when exposed to the air or even in closed containers, such as are used for storing laboratory samples. The changes are not solely due to oxidation, because of the presence of an anhydride. In six weeks the acid value had fallen 8 units, the

⁶¹ *Helv. Chim. Acta*, 1923, **6**, 214; *J.*, 1923, 278A.

⁶² *J. Amer. Chem. Soc.*, 1923, **45**, 1339; *J.*, 1923, 666A.

⁶³ Steele, *J.*, 1922, 558A.

⁶⁴ Knecht and Hibbert, *J.*, 1919, 472A.

⁶⁵ *Brennstoff-Chem.*, 1923, **4**, 246; *J.*, 1923, 939A.

⁶⁶ *Ind. Eng. Chem.*, 1923, **15**, 576; *J.*, 1923, 1186A.

saponification value had increased by 8 units, and the iodine value had fallen 55 units. The softening point of the rosin had risen nearly 12°C . It is of importance for analysts to powder the rosin immediately before examination. The glyceryl esters of rosin are reviewed by A. Murray⁶⁷ and H. Wolff⁶⁸ and details for their preparation are given. The statement that the presence of zinc oxide, zinc dust, zinc carbonate, or a galvanised surface of the melting pot accelerates the esterification,⁶⁹ must be accepted with reserve, as the temperature of esterification is an important factor in the reaction.

The investigations on the changes of state from the aspect of aggregation and solubility form the subject of papers from several investigators. H. Wolff in an investigation of the solution of lac in sodium carbonate, borax, etc., has confirmed observations by A. P. Laurie and C. Ranken,⁷⁰ and concludes that the solution process is of the nature of peptisation in the presence of alkali and that hydrogen ions, acting as coagulants, cause the loss of solubility of bleached shellac, unless it is kept under water.⁷¹ M. de Keghel⁷² discusses the mechanism of polymerisation and depolymerisation of resins. The resins, when exuded from the tree, consist of acids and esters forming a disperse phase in a polyhydric alcohol sol (so-called copal oil) in the form of elements of irregular dimensions called "particles." Each particle consists of a nucleus (granule) of ultra-microscopic dimensions and a variable number of molecules of esters and acids. The particles possess Brownian movement and the granules tend to join together, the surrounding layers of esters and acids disintegrating thereby. These changes constitute maturation. When they have proceeded far enough the resin sets to a soft mass and the colloidal state is destroyed. The subsequent hardening is due to the polymerisation of the esters; the degree of hardness depends on the state of polymerisation reached. Time, temperature, and pressure are secondary factors. By heating under conditions to prevent dissociation the resins can be softened to practically the same condition as when they were flocculated. If the softened resins be heated in water in an autoclave at gradually increasing pressures and for progressively increasing lengths of time they can be heated far above their initial melting point without any signs of incipient fusion or deformation and change in colour, but with a decrease in the acid value and saponification value and increase in iodine value and softening temperature. Demerara resin after several treatments at 344°C . and 38 atm. for 300 hrs

⁶⁷ *Oil and Col. Trades J.*, 1922, 2016.

⁶⁸ *Farben-Zeit.*, 1922, 27, 2020.

⁶⁹ U.S.P. 1,395,874.

⁷⁰ *J.*, 1917, 1242.

⁷¹ *Oil and Col. Trades J.*, 1923, 1002.

⁷² *Rev. Prod. Chim.*, 1923, 28, 109.

acquires values approaching those of amber. De Keghel infers that the various resins are of the same nature, but have reached different stages of polymerisation. C. Harries⁷³ suggests the use of the terms aggregation and disaggregation to replace polymerisation and depolymerisation. Harries and W. Nagel⁷⁴ have described two forms of purified shellac resin, identical structurally, but differentiated only in the state of aggregation, one form being easily soluble in alcohol and easily hydrolysed by alkali, whereas the other form is insoluble in alcohol and hydrolysed with difficulty. The forms are interchangeable by reagents, e.g., acetic acid will transform the inactive into the active form, whereas the active modification is made inactive by ether containing a little hydrogen chloride. The inability of one product to enter into chemical change is attributed to the mechanical arrangement of the particles in such a manner that an inadequate point of attack is offered to the reagent. The vulcanisation of rubber is attributed to the displacement of the aggregation of the particles. The alteration of dispersion of resins in solution by small quantities of reagents is well known, but the observations of Harries and Nagel are of interest in showing differences in the chemical properties of states of aggregation of a resin.

H. D. Wright and W. O. Kermack⁷⁵ state that the power of gelatin to protect gum benzoin against precipitation by sodium chloride solution depends on p_h and is at a minimum at the isoelectric point. Precipitation by acids depends essentially on the concentration of the hydrogen ions. The amount of salts required to precipitate the gum increases with the hydrogen ion concentration.

H. Dubovitz⁷⁶ has examined changes in the values of oil when destructively distilled to yield the stearine pitches. The composition of the pitch is undecided, although the conclusion as to the presence of characteristics of the fatty oil in the pitch holds true.

Rubber latex precipitates and dispersions are of interest to all manufacturers of water paints, and a study of their properties is worthy of consideration. Some notes on the Calvert process⁷⁷ show that the latex may be treated in such a way that the particles are retained in the subdivided form in which they exist in the latex. Each particle becomes coated with a condensate of the natural serum.

To those interested in the properties of the hydrogenated products of benzene, naphthalene (e.g., hexahydro-phenols and -creosols, hexaline and heptaline, tetra- and deca-hydronaphthalenes), useful

⁷³ Ber., 1923, 56, 1048; J., 1923, 612A.

⁷⁴ Ber., 1922, 55, 3833; J., 1923, 105A.

⁷⁵ Biochem. J., 1923, 17, 635; J., 1923, 1080A.

⁷⁶ Chem.-Zeit., 1923, 47, 616; J., 1923, 896A.

⁷⁷ Chem. Age, 1923, 328.

summaries of their properties are given by N. Heaton⁷⁸ and Wels-wark.⁷⁹ The valuable properties of these solvents make their investigation a matter of importance, and the initial difficulties with regard to their use will be overcome. Hexaline and heptaline possess the property of forming clear mixtures with aqueous soap solutions of the usual fatty acids, which mixed solutions possess remarkable solvent and emulsifying powers for fats, fatty acids, mineral oils, or waxes. It must be mentioned that a colour reaction for decaline in turpentine is unknown and 4% is the minimum amount which can be detected by the use of Salvaterra's method.⁸⁰

Synthetic Resins.

Progress in the manufacture of the phenol resins is the subject of a paper by L. V. Redman.⁸¹ He describes the application of laminated phenol products, Bakelite-Dilecto, Bakelite-Micarta, Laminated-Redmanol, Formica, Condensite-Celeron, and Fibroc, for the manufacture of octagonal plating-barrels in cyanide solutions and non-conducting conveyor-chains in cyanide plating. The laminated phenol products have sufficient resistance to cyanide solutions to give good life and wear in this mechanical-chemical operation. The pure phenol resins are unaffected by hydrofluoric acid and furnish transparent vessels for measuring cylinders and conductivity cells for acid. The woven laminated phenol resins are rapidly replacing other materials for silent gears, for resisting dampness and the corrosive effects of cleaning materials, and replace raw hide gears wherever rodents are a possible menace. They are also used in accurate gears for vernier adjustments on high-class radio phonographic motors and in printing presses. In the automatic telephone the laminated phenol resin products have replaced hard rubber as the insulation used in automatic piles, since the phenol resins when properly made have no "cold flow." These mechanical properties of rigidity or non-flowing under pressure from bolts and screws have given the phenol resins a very extended use in the radio industry. A further interesting mechanical application is the replacement of porcelain by phenol plastics, wherever violent shock is liable to break porcelain, as in the discharge of high-power guns on battle-ships.

In order to establish the proper temperature of "curing" of the phenol resins, the General Electric Co.⁸² incorporate a dye in the resin which undergoes change in colour as the temperature rises.

⁷⁸ *J. Oil and Col. Chem. Assocn.*, 1923, 6, 93.

⁷⁹ *Chem. Trade J.*, 1923, 305.

⁸⁰ H. Wolff, *Farben-Zeit.*, 1923, 29, 76.

⁸¹ *Ind. Eng. Chem.*, 1923, 15, 677.

⁸² E.P. 195,559; *J.*, 1923, 509A.

L. Behrend⁸³ states that the Albertole resins have proved as satisfactory as natural resins for the production of oil or other varnishes. An interesting development in the manufacture of synthetic resins is communicated by F. Folchi,⁸⁴ who has condensed naphthalene with formaldehyde and concentrated sulphuric acid at 80° C. The condensation product obtained is soluble in turpentine.⁸⁵ The furfural resins are reviewed by J. P. Trickey, C. S. Miner, and H. J. Brownlee,⁸⁶ who gives a general survey of the subject and of the use of acid and alkaline catalysts.

Furfural and phenol with hydrogen chloride as condensing agent give insoluble and infusible resins. Aniline with an alkaline condensing agent gives a resin soluble in alcohol, which stains wood a mahogany colour. A. Dobuis⁸⁷ gives a review of the synthetic resins prepared by the action of aliphatic aldehydes with aromatic hydrocarbons, amines, and phenols. The number of patents issued during the year is large. Farbw. vorm. Meister, Lucius, u. Brüning⁸⁸ are, perhaps, the most important contributors; their specifications comprise condensation products from ethyleneglycol monoaryl esters and condensation products of phenols with aldehydo- and keto-carboxylic acids, and formaldehyde with aryloxyacetic acids, also aromatic hydrocarbons with formaldehyde and other aldehydes. The ethyleneglycol monoaryl esters with formaldehyde give resins valuable in the rubber industry for conferring elasticity on other synthetic resins. There are recent patents involving condensation of methylene chloride and phenol,⁸⁹ formaldehyde and urea, thiourea, etc.,^{90 91} formaldehyde condensation products with phenols using sodium thiosulphate as condensing agent,⁹² and resins from glycerol and dibasic acids.⁹³ A connexion between resinification and chemical constitution has been investigated by W. Herzog and J. Kreidl.⁹⁴ They indicate the presence of resinophoric groups, C : C.C : C, N : C : C : and : C : C.C : N. For example, dibenzylidene-acetone when heated to 180° C. in carbon dioxide gives a resin; phenylketimine,

⁸³ Z. angew. Chem., 1923, **36**, 242.

⁸⁴ Rev. Chim. Ind., 1923; Oil and Col. Tr. J., 1923, 637.

⁸⁵ Cf. A. Hutin, Rev. Prod. Chim., 1922, **25**, 797.

⁸⁶ Ind. Eng. Chem., 1923, **15**, 65; J., 1923, 278A.

⁸⁷ A. Dobuis, Rev. Chim. Ind., 1923, **32**, 185, 211; Oil and Col. Tr. J., 1923, 1858.

⁸⁸ J., 1923, **6**, 613A, 614A.

⁸⁹ Holzverkohlungs-Ind. A.-G., E.P. 196,265; J., 1923, 939A.

⁹⁰ F. Pollak, E.P. 171,094; J., 1923, 509A.

⁹¹ E.E., 181,014; J., 1923, 988A; J., 1923, 940A.

⁹² J. G. Byrom and R. Attwater, E.P. 192,941; J., 1923, 318A.

⁹³ The Barrett Co., E.P. 173,225; J., 1923, 667A.

⁹⁴ Z. angew. Chem., 1922, **35**, 465, 841; 1923, **36**, 471; J., 1922, 771A, 989A; 1923, 1032A.

$\text{C}_4\text{H}_5\text{N} : \text{C} : \text{CH}_2$, is easily resinified, likewise acroleinmethylamine, $\text{CH}_2 : \text{CH}.\text{CH} : \text{NH}_3$, is readily polymerised.

A. Eibner⁹⁵ reviews the investigation of the relationships between resinification and chemical constitution as well as the general development of the artificial resins. An interesting summary of the manufacture and properties of the coumarone resins is given by E. Farber.⁹⁶ It must be pointed out that the purified resins as ingredients of lacquers, paints, varnishes, and printing inks must be completely free from sulphuric acid. Although 10,000 tons was produced annually in Germany during the war, there has been a marked reduction in output of late. Nevertheless, the polymerisation of coumarone and its associate substances can be effected in so many ways and lead to the formation of such divergent products as to offer a wide field of research for placing on a scientific basis the laws governing the empirically established processes of manufacture.

E. Knoevenagel and K. König⁹⁷ describe the conversion of solutions of cellulose acetate by small quantities of sulphuric or sulphoacetic acid, in the complete absence of moisture, into an insoluble modification with little or no loss of acetyl value and a slight decrease in the copper value.

PIGMENTS AND PAINTS.

J. Milbauer and K. Kohn⁹⁸ have continued their investigations on the conditions of production of chromo yellow. In an earlier communication the authors investigated the system: $\text{PbSO}_4 + \text{K}_2\text{CrO}_4 \rightleftharpoons \text{PbCrO}_4 + \text{K}_2\text{SO}_4$, and concluded that the interaction proceeded almost completely from left to right and that the existence of lead sulphochromates in the pigment was unlikely. It has now been shown that the brightest preparations are obtained if a solution of lead nitrate or acetate be added with constant stirring to a dilute solution of potassium chromate and potassium sulphate or sulphuric acid and the precipitate quickly separated from the mother liquor. The precipitate immediately after formation bears a definite relation to the contents of the original solution, the ratio $\text{PbCrO}_4/\text{PbSO}_4 : \text{K}_2\text{CrO}_4/\text{K}_2\text{SO}_4$ being constant. The precipitate consists of minute rhombic mixed crystals of lead sulphate and chromate, and the characteristic brightness of the product is due to the formation of a solid solution of these two compounds. It is important to encourage rapid separation and washing of the precipitate to preserve the lead sulphate from the

⁹⁵ *Z. angew. Chem.*, 1923, **36**, 33.

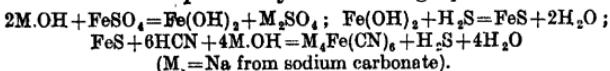
⁹⁶ *Metallbörse; Oil Col. Tr. J.*, 1923, 1858.

⁹⁷ *Cellulosechem.*, 1922, **3**, 113; *J.*, 1923, 140A.

⁹⁸ *Chem.-Zeit.*, 1922, **46**, 1145; *J.*, 1923, 105A; *J.*, 1916, 972; *Oil Col. Tr. J.*, 1923, 640.

action of chromate ions in the mother-liquor. The darkening of the pigment is attributed usually to hydrolysis of the lead chromate, but no satisfactory explanation has been given as to why lead sulphate reduces hydrolysis and contributes to the fastness to light of the pigment; perhaps it is more correctly attributed to the formation of isomorphous mixtures and solid solutions of lead sulphate and chromate, as shown by microscopical studies of the crystals and of the action of various solvents thereon.

A patent for the preparation of chrome pigments appears under the name of N. Underwood.⁹⁹ E. Renkowitz¹⁰⁰ has shown that the ignition temperature of chrome green containing 20% of Prussian blue and 80% of lead chromate is lower than that of mixtures containing more or less blue pigment. The addition of 2% of vaseline oil to the green pigment increases the ignition temperature beyond the danger point, i.e., 238° to 246° C.; the same rise in temperature is caused by the addition of large quantities of inert material, such as barium sulphate. The temperature of ignition of Prussian blue is 234° C., and the addition of small quantities of ferrous sulphate lowers the ignition temperature. Of all the processes for the manufacture of Prussian blue that for direct production from coal gas is claimed by A. Delclèvre¹⁰¹ to be the cheapest. The principle of the method can be expressed by the following equations:—



In order to avoid harmful secondary reactions, air is bubbled vigorously through the suspension of ferrous sulphide and the ferrocyanide, whereby the ferric oxide and sulphur formed are separated. The coal gas used must be free from ammonia. It is claimed that the process recovers the whole of the hydrogen cyanide, and avoids in the iron oxide purification mass the formation of compounds inert to hydrogen sulphide and the production of valueless thiocyanates.

The discussion on the darkening of lithopone and zinc sulphide still continues, and the investigations by several workers published during the year indicate progress towards the attainment of a generally satisfactory explanation. A. Job and G. Emschwiller¹⁰² consider that the darkening of zinc sulphide is dependent on the phosphorescence and hygroscopicity of the sample and is due to the formation of zinc and sulphur. Hydrogen and zinc pentathionate are also formed, hydrogen sulphide being an intermediate product. On the other hand, A. Schleede¹⁰³ states that there is no

⁹⁹ U.S.P. 1,441,612; *J.*, 1923, 235A.

¹⁰⁰ *Farben-Zeit.*, 1923, 28, 1066; *J.*, 1923, 509A.

¹⁰¹ *Chim. et Ind.*, 1923, 10, 632; *Abstr.*, 1924, B, 5.

¹⁰² *Comptes rend.*, 1923, 177, 313; *J.*, 1923, 897A.

¹⁰³ *Z. physik. Chem.*, 1923, 106, 386; *J.*, 1923, 1233A.

PAINTS, PIGMENTS, VARNISHES, AND RESINS

relationship between capability of blackening and phosphorescence. Pure zinc sulphide blackens very little, but the presence of chlorides facilitates darkening.

Steinau¹⁰⁴ considers that the presence of a chloride is essential to the production of a lithopone with good physical properties. The purification and preparation of the zinc solution is a very important stage in the manufacture of lithopone, deciding the whiteness of the product, whilst the covering power and softness are governed by the precipitation and calcination processes. The tendency of lithopone to blacken is due, according to Schleede, to the sulphide and halide crystallising together. When zinc sulphide is exposed to ultra-violet light it always blackens, irrespective of the percentage of halogen and heavy metal, if the sulphide be of a crystalline nature.

E. Maas and R. Kempf¹⁰⁵ consider that none of the hypotheses put forward is completely explanatory. They maintain that the blackening of lithopone is due to calcined zinc sulphides and conclude that the phenomenon is caused by the zinc sulphide forming zinc disulphide and finely divided metallic zinc on the surface of the mass.¹⁰⁶ Blackened lithopone brightens in the dark due to the oxidation of the metallic zinc, but the lithopone remains black if no oxygen be present. Amorphous, freshly precipitated zinc sulphide is not sensitive to light, neither is zinc sulphide which has been ground in a mortar, because this treatment would disturb the lattice arrangement of the substance. A. Eibner¹⁰⁷ states that the presence of chlorine is not the cause of the darkening of lithopone, but it decreases the light-proofness by combination with heavy metal impurities to form sensitive sulphochlorides. The discolouration of lithopone in light is strictly a chemical reaction caused by the phosphorescence of calcined zinc sulphide in actinic illumination, which in turn catalyses the formation of coloured sulphides of heavy metal impurities. The bleaching of lithopone discoloured by light occurs through the oxidation of the heavy metallic impurities. Light-proofness is obtained by removing from the original zinc solutions all heavy metal impurities.

It would appear as if the blackening of lithopone were connected with the presence of heavy metallic impurities and the degree of calcination of the zinc sulphide, but further investigations are required to establish unanimity as to the causes of the blackening.

* The literature on the titanium pigments includes a paper by

¹⁰⁴ *J.*, 1922, 65A.

¹⁰⁵ *Z. angew. Chem.*, 1922, 35, 609; 1923, 36, 293; *J.*, 1922, 94A; 1923, 729A.

¹⁰⁶ Cf. K. Fajans, *J.*, 1923, 245A, and E. Renversade, *J. Pharm. Chim.* 1923, 27, 458; *J.*, 1923, 729A.

¹⁰⁷ *Chem.-Zeit.*, 1923, 47, 13; *J.*, 1923, 150A.

E. O. Rasser,¹⁰⁸ who reviews the present knowledge of the pigments.¹⁰⁹ He states that they are inactive towards oil and to pigments used in paint and varnish industries. No mention is made in the literature of the titanium pigments of the oxygen-absorbing powers of the titanium dioxide salts, with the production of the yellow higher oxides, especially in the presence of hydrogen peroxide. The production of titanic acid is the subject of patents by C. Weizmann and J. Blumenfeld.¹¹⁰ The last traces of iron from the ilmenite product are removed by washing the precipitated titanium hydroxide with acidified water containing a small quantity of the salts of trivalent titanium. H. Olsen¹¹¹ in a review of the subject states that titanium paints are almost unaffected by weather and acid vapours.

The use of titanium pigments has stimulated interest in the determination of the metal. L. E. Barton¹¹² gives a method for determining barium sulphate and titanium dioxide in "titanox," with directions for the analysis of mixed pigments containing titanium.

In the manufacture of zinc oxide the coloured oxides of lead and cadmium can be removed by adding sulphuric acid and roasting not above 820° C. for 30 minutes. Basic zinc sulphate decomposes at 755° C., whilst $6\text{PbO}, 5\text{SO}_3$ and $5\text{CdO}, 4\text{SO}_3$ decompose at 878° C.¹¹³

The value of the vermilion produced in China (Hong-Kong) is 1,800,000 Hong-Kong dollars. The industry is one of the oldest and best known in China and 90% of the output is used in the country.¹¹⁴

In connexion with the problem of the poisonous action of lead in paints; J. J. Fox¹¹⁵ has communicated a paper on the solubility of lead compounds used in paints. An order of the Secretary of State under the Act of 1920 lays down that "lead compound shall mean any compound of lead other than galena, which when treated at the ordinary temperature with 1000 times its weight of hydrogen chloride (0.25%) shall yield a quantity of soluble lead compound exceeding 5% (calc. as PbO) of the portion taken for analysis." This requirement has been effective in the pottery industry in dealing with lead silicates, but its application to the paint industry is open to criticism in view of the preponderating influence of the dust factor in lead poisoning. It must be admitted that the Government limit of 5% is more generous than the percentage (2%)

¹⁰⁸ *Chem.-Zett.*, 1923, 47, 460 : *J.*, 1923, 729A.

¹⁰⁹ *J.*, 1922, 216R.

¹¹⁰ E.P. 203,352 ; *J.*, 1923, 1070A.

¹¹¹ *Edel-Erden u. Erze*, 1923, 4, 1.

¹¹² *Oil and Chem. Rev.*, 1923, 75, 10.

¹¹³ *Oil and Col. Tr. J.*, Dec. 2, 1922.

¹¹⁴ *Compt. Tr. J.*, 1923, 615.

¹⁰⁸ *Z. physik. d. Col. Chem. Assoc.*, 1923, 6, 129.

agreed on between the master painters and the Home Office, especially when red lead was not included among lead compounds (Annual Report, 1923).

The Report of the Home Office Committee¹¹⁶ contains a number of recommendations and conclusions, some of which are subversive of the labours of previous committees. For outside painting and for certain kinds of inside painting there is at present no efficient substitute for lead paint. The Geneva Convention is recommended for legislative sanction with some modifications and regulations to deal with the combined use of lead paints. The cumulative effect of the evidence since 1913 is that there has been a marked increase of cost involved in the maintenance of external surfaces painted with a non-lead paint. The Committee is satisfied that the dangers attendant upon the use of lead paint can be minimised by regulations providing for the abolition of dry "rubbing down," for adequate arrangements for personal cleanliness and, where necessary, for medical examination of the workers. Another conclusion is that there is not sufficient ground to warrant accepting the view that turpentine poisoning is the cause of the leading symptoms commonly attributed to either acute or chronic lead poisoning, nor in attributing to the inhalation of the fumes of turpentine and other thinners the occurrence of Bright's disease. The results of this and other committees have stimulated the adoption of reasonable safeguards¹¹⁷ and have done much to encourage the investigation of possible substitutes for lead, whereby new materials have come into use without displacing largely the older substances and have brought to light new properties of pigments and widened their choice. Control, rather than prohibition, appeals to British thought, but control must be efficient and not irksome, otherwise prohibition must win where the safety of any section of the community is involved. F. Heim, E. Agasse-Lafont, and A. Feil¹¹⁸ state that lead and its compounds and not turpentine are the habitual cause of renal lesions and hypertension in painters.

The preparation of lead sulphate oil paste is the subject of a patent by D. Whyte, in which it is claimed that precipitated lead sulphate, dried to remove the bulk of the water, when churned with about 9% of oil loses its water of crystallisation and forms with the oil a smooth paste. The details of the patent apply to precipitated lead sulphate.¹¹⁹

H. Green¹²⁰ has improved the method of obtaining photomicrographs ($\times 1500$) of pigments.¹²¹ He claims that American-process

¹¹⁶ *Chem. and Ind.*, 1923, 376.

¹¹⁷ C. A. Klein, *J. Roy. Soc. Arts*, 1923, 71, 240; *J.*, 1923, 318A.

¹¹⁸ *Comptes rend.*, 1923, 176, 270; *J.*, 1923, 235A.

¹¹⁹ E.P. 191,886; U.S.P. 1,419,655; *J.*, 1922, 600A.

¹²⁰ *Chem. and Met. Eng.*, 1923, 28, 53; *J.*, 1923, 277A.

¹²¹ *J.*, 1921, 896A.

zinc oxide can be distinguished from French-process zinc oxide, and gives the average diameter of the particles of a number of pigments.

Attention continues to be drawn to the applications of the colloid mill. Reference to the Plauson mill was made in the previous Annual Report and a further description is to be found in a paper by W. J. Kelly.¹²² The Premier mill¹²³ is not designed for producing true colloids; it is really on the principle of a rapidly revolving cone-mill, so that the film of liquid is actually sheared under conditions, which do not permit of the liquid acting as a fluid but as a solid, and that the particles in the line of shear must themselves become disintegrated during the shearing. The presence of protective substances is necessary to prevent coalescence of the particles. It is not claimed that the Premier mill can reduce solids to the colloidal state, which can only be attained by means of the Plauson mill, but in the Premier mill large quantities can be dealt with. It is not every pigment that will give satisfaction, but in the case of the softer varieties, such as are used for enamels and printing inks, a process is available whereby 20–60 gals. per hour can be dealt with.

The colloidal phenomena in paints are discussed by C. Coffignier¹²⁴ in reference to the thickening of paints and the advantages of using esters of the resin acids. The insolubility of the esters of copals in oils often presents difficulties. E. B. Spear and H. A. Endres¹²⁵ have made a critical study of the obscuring-power method for determining the relative average size of pigment particles. A method of preparing micro-sections of paints is described by H. L. Maxwell.¹²⁶ The number of coats of white lead or zinc paints making up a film can only be determined by staining the section with mildly alkaline methylene blue.

There are several papers of interest dealing with the hiding power of thinners. R. L. Hallett¹²⁷ states that the hiding power of a pigment is a geometric function of paint film thickness, and he obtained additional confirmation by measurements on panels to which paint had been applied at such a rate that the thickness of the film and the amount of pigment on the panels varied at a constant rate. Tinting-power experiments made by rubbing up white pigments with lampblack show that hiding and tinting powers are direct measures of each other.

A. H. Pfund¹²⁸ finds that within the brightness range of 75–85%, using values of hiding power measured by his cryptometer¹²⁹ and

¹²² *Ind. Eng. Chem.*, 1923, **15**, 927.

¹²³ *Chem. Age*, 1923, 329.

¹²⁴ *Bull. Soc. Chim.*, 1923, **38**, 128; *J.*, 1923, 278A.

¹²⁵ *Ind. Eng. Chem.*, 1923, **15**, 725; *J.*, 1923, 841A.

¹²⁶ *Chem. and Met. Eng.*, 1923, **28**, 850; *J.*, 1923, 612A.

¹²⁷ *Proc. Amer. Soc. Testing Materials*, 1923, **22**, II., 523.

¹²⁸ *J. Franklin Inst.*, 1923, **196**, 69; *J.*, 1923, 841A.

¹²⁹ *J.*, 1920, 34A.

the brightness values recorded by his colorimeter,¹³⁰ the ratio of the increase in hiding power to the percentage decrease in brightness equals 5·0 for all white paints. At complete hiding a grey paint film is far more transparent than a corresponding white film. Opacity measurements must be used with caution in drawing conclusions as to hiding power.

H. A. Gardner and P. C. Holdt,¹³¹ using Pfund's instruments, have studied the relations between brightness, opacity, and approach to pure whiteness of pigments and paints. The addition of ultramarine to paints containing very bright pigments, which are low in blue brightness, decreased their brightness slightly, but makes them far more nearly non-selective and increases greatly their hiding power. The limitations of the obscuring power method of determining the size of pigment particles are pointed out by E. B. Spear and H. A. Endres.¹³²

The investigations on the properties of plastic flow have been continued by E. C. Bingham and H. Green, with collaborators, and their results have been criticised by A. de Waele. A brief summary of the results and criticisms are of interest. E. C. Bingham¹³³ concludes that suspensions share with emulsoid colloids the properties of plasticity at very low concentrations of the disperse phase, and distinguishes between true plasticity at high volume concentrations and pseudoplasticity at low concentrations, when the yield value-concentration relationship is not linear. The transition from the pseudoplastic to the plastic state occurs in the case of lithopone and linseed oil when the mixture contains 14% of lithopone, and when the mixture contains 45·6% by volume of lithopone the mobility is zero. In a later paper¹³⁴ the results are confirmed, and the effects on mobility and yield values of paints produced by long grinding, by alteration in the concentration of the pigment, addition of water, mineral oil deflocculating agents, etc., were measured and tabulated. The yield value of silica-lithopone is independent of the fluidity of the oil, but aluminium stearate increases the yield value, as likewise moisture (0·3%) with a reduction in mobility by three-quarters of its value. The same author and collaborators¹³⁵ state that by means of the plastometer it is possible to distinguish between colloidal solutions, exhibiting yield value, and true solutions, also between polar (nitrocellulose in acetone) and non-polar (simple oil paint) colloidal type. In the polar type rise in temperature reduces yield value, whereas in the non-polar type the yield value is,

¹³⁰ *Ann. Repts.*, 1921, 6, 338.

¹³¹ *Paint Manuf. Assoc., U.S.A.*, Circ. 173; *J.*, 1923, 463A.

¹³² *Ind. Eng. Chem.*, 1923, 15, 725; *J.*, 1923, 841A.

¹³³ *J. Franklin Inst.*, 1923, 195, 303; *J.*, 1923, 385A.

¹³⁴ *Ind. Eng. Chem.*, 1923, 15, 1023; *J.*, 1923, 1185A.

¹³⁵ *Ibid.*, 1922, 14, 1014; *J.*, 1923, 38A.

unaffected. H. Green¹³⁶ states that there are four factors on which the consistency of paints depends, especially that of flocculation in the pigment-vehicle system. Following a discussion on the forces of flocculation, its influence on the yield value and mobility, together with the great change in paint consistency which can be brought about by the presence of a heavy-bodied oil, e.g., poppy-seed oil, they conclude that it is impossible to produce paints with the same yield value and mobility, one of which is stringy and the other not. The stringiness of paints is attributed to deflocculation or increased "wetting," resulting from slight oxidation, and it can be fully defined in terms of yield value and mobility. A. de Waele¹³⁷ criticises the work of Bingham and his collaborators as based on insecure foundations, in that the curvature of relationship between pressure and velocity has been interpreted as slippage. He gives a mathematical disproof of the relationship expressing Bingham's law of plastic flow $(P-p)/Q=\text{constant}$. The interpretation of the properties of a plastic may be expressed as follows: $P\phi=Q\zeta$ where ϕ is a fractional exponent representative of the degree of plasticity in the value of $1-\phi$, and ζ represents a function of viscosity.

$$\phi = \frac{\log P_2 - \log P_1}{\log Q_2 - \log Q_1}; \quad \zeta = \log P_2 - Q_1 \log Q_2$$

Bingham and Green strongly criticise the conclusions in the above paper, to which de Waele replies by reference to the work of Porst and Moskowitz¹³⁸ and Herschel and Bergquist,¹³⁹ as a confirmation of the statement that the validity of the Bingham-Green formula has failed to be substantiated.

In the investigation concerning the loss and changes of colour of pigments when exposed to or protected from light, A. Eibner¹⁴⁰ ascribes to the formation of free linolenic acid or its peroxide the cause of the yellowing of linseed oil films in moist air protected from light. S. F. Harmer¹⁴¹ has carried out experiments to observe the loss of colour in paints illuminated by daylight or electric light and the efficiency of various tinted glasses in preventing such loss. The periods of exposure were 1030 and 1485 days respectively. In general the results of Abney were confirmed, and it was shown that fugitive colours will not fade in a strong light if protected completely from oxygen and moisture. It is suggested that a certain intensity or quality of illumination is required to initiate the process of fading.

¹³⁶ *Ind. Eng. Chem.*, 1923, **15**, 122; *J.*, 1923, 277A.

¹³⁷ *J. Oil and Col. Chem. Assoc.*, 1923, **6**, 23.

¹³⁸ *Ind. Eng. Chem.*, 1922, **14**, 19.

¹³⁹ *Ibid.*, 1921, **13**, 703.

¹⁴⁰ *Bayer. Ind. Gewerbeblatt*, 1922, **64**, 105; *J.*, 1923, 190A.

¹⁴¹ *J. Roy. Soc. Arts*, 1923, **71**, 144; *J.*, 1923, 151A.

M. de Keghel¹⁴² contributes a very interesting article on the uses of casein in the paint industry. Considerable attention has been paid to the investigations on the unsatisfactory value of marine anti-fouling and anti-corrosive paints. The experience of U.S. Navy research on ship-bottom paints decides in favour of a shellac varnish paint containing turpentine, pine oil, zinc oxide, and zinc dust as an anti-corrosive coating. For anti-fouling composition a similar paint containing Indian red and mercuric oxide, instead of zinc dust, is recommended. H. A. Gardner¹⁴³ finds that the anti-fouling solution referred to above gave very poor results, whereas copper compounds were more satisfactory and ester-gum paints proved more reliable than those containing shellac. The tests did not always indicate a relation between barnacle resistance and toredo action, but emphasised the importance of destroying the embryos.

P. E. Bowles¹⁴⁴ recommends as anti-corrosive coatings solutions of pitches and asphalts incorporated with iron oxide pigments; for anti-fouling compositions he recommends solutions of resins ground with oxides of iron and salts of copper or mercury. Arsenic is useless, except in complex compounds with copper, and mercury is best in the form of organic salts, rather than as chloride.

The summary of these investigations does not indicate success in solving what is an important problem.

VARNISHES.

Insulating varnishes offer great possibilities of variation in quality and behaviour, and unless carefully checked and tested in the laboratory are likely to cause trouble and expense, especially if each new batch requires some alteration in the factory routine to give satisfactory results; such is the opinion of A. A. Drummond.¹⁴⁵ He recommends the determination of a number of properties of a fluid varnish, e.g., penetrating power, flexibility, heat insulation, and resistance to the action of chemicals etc. The requirements of insulating varnishes apply to insulating compositions for moulding work from ordinary pitch and asbestos to the more efficient products with the higher-melting resins, especially the phenol-formaldehyde varieties. With such compositions the properties of softening point, inflammability, and water absorption must be examined. It is now easy to obtain resins suitable for impregnating coils in such a condition that the final non-reactive state can be attained at lower temperatures and at atmospheric pressure with less elaborate plant. In the brief and general survey of some of the chemical

¹⁴² *Rev. Produits Chim.*, July, 1923.

¹⁴³ *Paint Manuf. Assoc.*, Circ. 157, 1922, and Circ. 176, 1923.

¹⁴⁴ *J.*, 1922, 492R.

¹⁴⁵ *Chem. and Ind.*, 1923, 769.

problems connected with electrical industry, attention is drawn to the necessity of making use of chemical knowledge in a realm where engineering has held sole sway.

The General Electric Company¹⁴⁶ has patented an insulating composition consisting of mica, impregnated with an acetone solution of a reaction product of glycerin and phthalic anhydride, which after stoving at 300° C. is insoluble in water and linseed oil. H. C. Weber¹⁴⁷ points out that the lowering of electric resistance, consequent on drying of insulating oil varnishes, is caused by the oil acids.

The application of varnishes by spraying or by brushing is considered best as a compromise of the two methods.¹⁴⁸ The use is recommended of a spray brush, *i.e.*, a hollow brush in the centre of which the paint or varnish is delivered under air pressure in the form of fine spray or a brush automatically supplied with paint or varnish.

An experimental drying time tester for varnishes has been devised by H. A. Gardner,¹⁴⁹ consisting of a clock-operated drum, which winds on to itself a blank moving-picture film, coated with varnish and a strip of tissue paper. The paper strip is brought into contact with the varnish film just as it is drawn on to the drum. The drying time is measured to the point where the paper ceases to adhere or becomes stained by the varnish film.

J. Scheiber and O. Nouvel¹⁵⁰ have determined the molecular weight of linseed oil in naphthalene or stearic acid and state that copals enter into combination with oil, whereas rosin in oil forms a true solution. It is difficult to accept the conclusions of these experiments, because of the marked difference between the acidity values of copals and rosin, which have a strong effect on their dispersive powers. It would be of interest to have values of ester gums in linseed oil.

E. O. Rasser¹⁵¹ considers that tetraline compared with turpentine as a thinner is a decided success. The general opinion is that tetraline is a good varnish thinner—too good in some respects—but its peculiar odour makes it undesirable at present for indoor varnishes. The pink discolouration of white enamel films, in which tetraline is a component, is considered by A. Leuffs¹⁵² to be due to the presence of manganese driers. Lithopone containing 0·005% of manganese and moistened with tetraline shows an unmistakable pink colour. Turpentine acts similarly, but is less sensitive.

¹⁴⁶ E.P. 203,232; *J.*, 1923, 1031A.

¹⁴⁷ *J. Amer. Chem. Soc.*, 1923, 44, preprint.

¹⁴⁸ *Circ.* 18, *Nat. Paint, Oil and Varnish Assoc., U.S.A.*; *J.*, 1923, 190A.

¹⁴⁹ *Paint Manuf. Assoc. U.S.A.*, *Circ.* 167; *J.*, 1923, 318A.

¹⁵⁰ *Z. angew. Chem.*, 1923, 36, 353; *J.*, 1923, 841A.

¹⁵¹ *Chem.-Zeit.*, 1923, 47, 660; *J.*, 1923, 898A.

¹⁵² *Ibid.*, 1923, 47, 315; *J.*, 1923, 809A.

In the testing of small quantities of varnishes, H. Wolff and C. Dorn¹⁵³ give directions for the examination of the solvents in which dispersion and refractive indices form a basis of a system of grouping. For the comparison of the rate of evaporation of the solvents on filter paper xylol is used as standard and the boiling point of the solvents can be observed, using a capillary tube. J. A. Findley¹⁵⁴ has attempted to develop uniform tests on a numerical basis for the relative merits of varnishes. A Report of a Committee of the American Society for Testing Materials contains results of testing varnishes by the kauri test, drying time, and effect of hot and cold water on the film. H. Wolff¹⁵⁵ lays stress on the great influence of humidity during the application and drying of varnishes on their durability. The effect of light and variation in temperature is not nearly so destructive as that of humidity. The concensus of opinion is in favour of Wolff's conclusions. The same author wisely maintains the undesirability of giving a guarantee with varnishes, owing to unforeseen weather conditions of application and use. The durability of the varnish film depends, not only on the nature of the material, but on the mode of application, as well as the preparation of the undercoat.

The failure of paint and varnish films on exposure to the weather is now engaging the attention of the experts on the U.S. Bureau of Standards. Some claim that a paint and varnish film should contain moisture in order to retain its elasticity, others hold that baking varnishes are more durable. It is most probable that for durability oxidation is essential and is more easily realised by the baking of the film. The experience of the U.S. Forest Service at the Forest Products Laboratory, Madison, Wisconsin, on the protection of wood is of interest, in that a coating of gloss oil and aluminium powder was superior to enamels, oil paints, and varnishes. The superiority of suitable aluminium paints is worthy of consideration. Among other coatings examined, spar-varnish coated with vaseline was nearly as good as an aluminium leaf process with an asphalt paint base, which is classed as the best of the list. Cellulose lacquers and white lead oil are much lower in the list.

The problem of the corrosion of metals, ferrous and non-ferrous, has received considerable attention during the year under review and the discussions form part of another report. Reference can only be made to those points in which the question of organic coatings arises. U. R. Evans¹⁵⁶ states that protection by means of paints is more efficient than protection by a covering of another

¹⁵³ *Farben-Zeit.*, 1922, 28, 330; *J.*, 1923, 62A.

¹⁵⁴ *Proc. Amer. Soc. Testing Materials*, 1922, I, 479, 375.

¹⁵⁵ *Farben-Zeit.*, 1923, 28, 704; *J.*, 1923, 277A.

¹⁵⁶ *Oil and Col. Tr. J.*, 1923, 1681.

metal. Corrosion-resisting alloys will not as yet invade classes of work in which paints are now used.

The minutes of the joint conference on corrosion problems conducted by the Faraday Society¹⁵⁷ are of interest in showing the corrosion which an organic coating is called on to prevent. The protection of a metal by a thin film of oxide often breaks down if other metals are present, as in the case of alloys; moreover, the thin film of oxide is sometimes fragile and requires an organic coating to complete the protection.

The much discussed question of oil varnish analysis has received attention during the year and evidences of progress in the acceptability of the results is shown, especially in the work of H. Wolff.¹⁵⁸ The author wisely states that the present-day analysis must satisfy the following requirements—the kind of oil, resin, solvent, and driers—and emphasises the limitation of the application of the quantitative results. It is difficult to build up a works recipe from the percentages of resin, oil, and thinners obtained from a quantitative analysis, even if that analysis can be accepted as reliable. The modification of the usual methods seems to be in the isolation of the free and inorganically combined fatty and resin acids. The external appearance of these acids should be noted and they may be tested by known reactions for colophony and for solubility in 85% alcohol, in which a copal gives a turbid solution in certain concentrations. The author considers that the amount of these components affords a valuable figure in judging varnishes. Later on, the unsaponifiable matter is separated from the oil and resin acids present as esters and anhydrides and the oil acids are examined for their refractive indices. The resin acids can be determined by Wolff and Scholze's method.¹⁵⁹

H. C. Coffignier endeavours to separate the oil and resin components of a varnish by oxidation at 100° C. and the removal of the resin by amyl alcohol, leaving the linoxyn undissolved. The author admits that the separation of the oil and resin is not strictly quantitative.¹⁶⁰

¹⁵⁷ See *Chem. Age*, 1923, 394.

¹⁵⁸ *Farben-Zeit.*, 1923, 29, 74; *J.*, 1923, 1080A.

¹⁵⁹ *J.*, 1914, 363.

¹⁶⁰ *Moniteur de la Peinture; Oil and Col. Tr. J.*, 1923, 465.

INDIA-RUBBER.

By B. D. W. LUFF, F.I.C.,

Research Chemist, North British Rubber Company, Ltd., Edinburgh.

DURING the past year the trade in manufactured rubber goods, other than tyres, has shown a marked improvement over that of 1922, but the demand for raw rubber has not yet overtaken the supply, and efforts are being made by the planters themselves to encourage the manufacture of new articles.

STATISTICS.

The rapid increase in importance of plantation rubber during recent years will be seen from the following figures, showing the relative production of wild and plantation rubber at intervals of 5 years.¹

| Year. | Plantation. | | Wild. | | Total. |
|---------|-------------|---------|--------|--------|---------|
| | Tons. | Brazil. | Tons. | Rest. | |
| 1907 .. | 1,000 | .. | 38,000 | 30,000 | 69,000 |
| 1912 .. | 28,518 | .. | 42,410 | 28,000 | 98,928 |
| 1917 .. | 213,070 | .. | 39,370 | 13,258 | 265,698 |
| 1922 .. | 354,980 | .. | 21,755 | 3,205 | 379,940 |

The country of origin of the plantation rubber is indicated by the following figures, which, however, are subject to certain modifications; for example, the amount exported from Malaya includes rubber originally imported from countries not mentioned in the returns.

Exports of Plantation Rubber, 1922.

| | | | | Tons. |
|---------------------------------|----|----|----|---------------------|
| British Malaya .. | .. | .. | .. | 248,158 |
| Java .. | .. | .. | .. | 31,558 |
| Sumatra (E. Coast only) .. | .. | .. | .. | 40,552 |
| Ceylon .. | .. | .. | .. | 47,367 |
| | | | | 367,635 |
| Deduct for transhipment etc. .. | .. | .. | .. | <u>12,655</u> |
| | | | | <u>Net total ..</u> |
| | | | | <u>354,980</u> |

The quantities of rubber absorbed by the leading consuming countries may be gathered from the statistics showing the amount retained during a period of three years.

| | 1920. | 1921. | 1922. |
|-------------------|---------|---------|---------|
| United States .. | 248,791 | 179,647 | 296,267 |
| United Kingdom .. | 56,972 | 42,116 | 11,164 |
| France .. | 16,606 | 14,701 | 27,680 |
| Germany .. | 13,400 | 22,428 | 27,551 |
| Canada .. | 11,300 | 8,2,9 | 9,353 |
| Japan .. | 5,500 | 23,164 | 16,581 |
| Italy .. | 6,300 | 4,000 | 6,500 |

¹ "The World's Rubber Position," Rickinson, London.

A proper appreciation of the actual consumption of the smaller consumers can be obtained only by taking into account the visible stocks at the beginning and end of the period. For example, stocks in warehouses in the United Kingdom increased by no less than 24,582 tons over the period indicated, so that the actual consumption would be considerably less than the amount of rubber retained.

By far the greater proportion of the rubber produced is utilized in the manufacture of tyres, as may be gathered from the fact that in America 83% of the rubber imported is absorbed by the automobile industry.²

Reference was made in the last report³ to the application of the Stevenson scheme for restricting the production of rubber in British Malaya and Ceylon. The effect of the scheme is reflected in the fact that the export of rubber from Malaya for the first 10 months of this year amounted to 155,905 tons, as compared with 182,363 tons during the corresponding period of 1922.⁴

The price of rubber increased steadily from the time of the introduction of the scheme, and for the quarter ending April 30, 1923, the average price was between 1s. 3d. and 1s. 6d. per lb. Owing to this price being maintained for three months, the percentage of standard production allowed for export was increased from 60% to 65% for the next quarter, in accordance with the provisions of the scheme. The exportable allowance was, however, reduced to 60% for the quarter beginning August 1st, and has remained at that figure since that date.

According to the report of the Rubber Controller for Malaya⁵, the total exportable allowance for the period November, 1922, to July, 1923, was 126,413 tons, corresponding to 60% of standard production from November, 1922, to April, 1923, and 65% from May to July, 1923, inclusive.

These figures are based on a standard production for the restriction area of 274,000 tons per annum. During this period of nine months the net exports amounted to 115,306 tons, this figure representing the total exported, less re-exports of rubber produced outside Malaya, and stocks in hand at the inception of the scheme.

The enforced restriction of the production of rubber has led to considerable apprehension on the part of American manufacturers, with the result that in some quarters the cultivation of rubber in the Philippine Islands has been advocated. This proposal has been made previously, and there are a few small plantations already in existence.⁶ Plans for the extensive cultivation of rubber in the Philippines have not met with unanimous approval. The question

¹ *Bull. Rubbers Growers' Assoc.*, 1923, 5, 79.

² *Ann. Repts.*, 1922, 7, 308.

³ *India Rubber J.*, 1923, 66, 801.

⁴ *Bull. Rubber Growers' Assoc.*, 1923, 5, 581.

⁵ Cf. Pearson, *India Rubber World*, 1917, 57, 3.

of rendering America independent of British and Dutch supplies of rubber has now been taken up by the United States Government, who have appointed a commission under the direction of Dr. H. N. Whitford, with the object of making a survey of the rubber-producing areas in Mexico, Brazil, and the Philippines.⁷

RUBBER LATEX.

The treatment of latex in countries outside the rubber growing areas⁸ appears to be rapidly progressing beyond the experimental stage, and the fact that large quantities of latex are now being dealt with by manufacturers will be evident from a consideration of the following figures representing the amount exported from the countries specified during 1922 and 1923.⁹

| Country of shipment. | Gallons of latex exported. | |
|----------------------|----------------------------|-----------------------|
| | 1922. | 1923. (Jan.-Sept.) |
| Malaya | 40,061 (a) | 72,728 |
| Ceylon | 1,977 (b) | 11,413 |
| Sumatra | 228,324 | 2,021,441 |
| Total | <u>270,362</u> | <u>2,105,582</u> |

(a) Seven months only; (b) Two months only.

The quantity exported up to the end of September, 1923, represents approximately 3390 tons of dry rubber, or a little more than 1% of the total plantation shipments of rubber for that period. It should be noted, however, that during September alone there was exported from Sumatra 950,000 gallons, equal to approximately 1480 tons of dry rubber, or about 4½% of the total amount of rubber shipped from all countries in that month. The export of such large quantities of latex from Sumatra may be traced to the fact that in the island are situated plantations owned by companies associated with the United States Rubber Company, holders of the patent rights of the Hopkinson process for spraying latex.¹⁰

While it is probable that the bulk of the exported latex is desiccated by a spraying process and the dry rubber utilised in the normal manner, it is possible that a proportion is being applied directly, as, for example, in the proofing of textiles in place of a rubber dough made with the aid of an organic solvent.¹¹

The interest aroused in proposals of this character is reflected in numerous communications concerning the preservation and transport of latex. Coagulation during shipment is usually prevented by

⁷ *Bull. Rubber Growers' Assoc.*, 1923, 5, 513.

⁸ *Ann. Repts.*, 1922, 7, 310.

⁹ *Bull. Rubber Growers' Assoc.*, 1923, 5, 590.

¹⁰ *Ann. Repts.*, 1922, 7, 312.

¹¹ *Ibid.*, 311.

adding ammonia, and results of experiments carried out by O. de Vries, N. B. Nieuwland, and R. Riebl¹² show that under favourable conditions the addition of 15 c.c. of aqueous ammonia (sp. gr. 0.9327) per litre of latex, giving a concentration of approximately 0.25% NH₃, is usually sufficient; a margin of safety should, however, be allowed, and this may be secured by adding 20 c.c. per litre. For the determination of ammonia in latex, titration with acid, using methyl red as indicator, is recommended. On keeping, the alkalinity, as determined in this manner, decreases slightly, and a sediment is deposited which contains crystals of ammonium magnesium phosphate together with rubber globules. The authors note certain points of difference between the coagulation of fresh and preserved latex. On the addition of acid to fresh latex, and also to freshly ammoniated latex, a compact clot is not formed until after the lapse of some time after the acid has been stirred in; with ammoniated latex which has been kept for a month or more the clot forms almost immediately. Similar observations have been made by H. P. Stevens,¹³ who notes that preserved latex is usually more mobile¹⁴ and does not adhere to the walls of the containing vessel in the same way as does fresh latex. Coagulation does not take place cleanly, and in some cases a partial coagulation sets in even before the ammonia present as preservative is completely neutralised. Latex preserved with caustic soda usually requires less acid than that preserved with ammonia, and coagulation often occurs instantaneously with the addition of acid of 0.5% concentration.

Preserved latex may be coagulated by adding inert powders in a fine state of division, such as colloidal clay or carbon black. According to C. C. Loomis and H. E. Stump,¹⁵ however, many compounding ingredients, such as clay, whiting, talc, may, if previously wetted, be added to latex in very high proportions, without causing coagulation, although zinc oxide and carbon black both result in coagulation even when small proportions are added. The coagulating effect of added fillers may be due to absorption of water which causes local concentration of the latex, or to the presence of a positive charge on the particles of filler neutralising the negative charge on the rubber particles, or by the material being sufficiently soluble to yield a solution which acts as a coagulant.

The tendency exhibited by preserved latex to "cream" has been commented on by H. P. Stevens,¹⁶ and it may be noted that the "cream" which collects on the surface of the latex is quite thick,

¹² Comm. Central Rubber Station, Buitenzorg, 1923, No. 33; J., 1923, 731A.

¹³ Bull. Rubber Growers' Assoc., 1923, 5, 511; J., 1923, 1082A.

¹⁴ Cf. O. de Vries, Comm. Central Rubber Station, Buitenzorg, 1923, No. 36.

¹⁵ Chem. and Met.-Eng., 1923, 29, 540; J., 1923, 1082A.

¹⁶ Bull. Rubber Growers' Assoc., 1923, 5, 216.

but on shaking with water re-forms an emulsion having the properties of normal latex.¹⁷ Attempts were made to induce the formation of "cream" by treatment in an ordinary milk separator, but it was found that, as a general rule, instead of a "cream" being formed, coagulation occurred. The tendency to coagulate is less apparent in ammonia-preserved latex than in that preserved with the aid of caustic soda and coal-tar derivatives.

The possibility of forming a "cream" in latex is important in connexion with the question of transportation, for, if this could be achieved and the cream separated, a concentrated latex would result. The cost of transport of the rubber in this form would therefore be considerably reduced, and the latex could be subsequently treated either in this condition or after diluting with water. Experiments on the concentration of latex have been carried out by C. C. Loomis and H. E. Stump,¹⁸ who state that this may be effected *in vacuo* after adding a trace of sodium carbonate or caustic soda, but there are objections to this procedure, among these being the fact that there is a tendency for a skin of rubber to form on the surface during evaporation.

The use of a centrifugal was found to give promising results, as a "cream" having a rubber content of 76% was obtained by means of a laboratory type of super-centrifugal running at 30,000 r.p.m. Trials on a large-sized machine running at 16,000 r.p.m. gave less satisfactory results, as latex with an initial concentration of 36% rubber gave a "cream" containing only 43.8% rubber, the weaker liquid still containing 31.9%. Diluting the latex gave a more concentrated "cream," but even in this case a very great proportion of the rubber remained in the dilute fraction. It was found, however, that the quality of the rubber in the two fractions differed very considerably; the concentrated portion of the latex gave a rubber possessing very good physical properties, whereas the dilute portion of the latex gave on coagulation a rubber possessing little strength. It is suggested that advantage may be taken of this fact in preparing rubber having special properties.

For the determination of rubber in latex H. P. Stevens¹⁹ concludes that the method previously recommended, consisting in evaporating and weighing the total solids²⁰ is not satisfactory, as the amount of non-rubber substances soluble in water varies considerably in different lots of latex. It is suggested that the best method would be to coagulate the latex, preferably with the aid of dilute sulphuric acid, and to convert the rubber to crêpe on a small experimental washing mill. In cases where acid does not effect a clean coagula-

¹⁷ Cf. de Vries, Nieuwland, and Riebl, *loc. cit.*

¹⁸ *Chem. and Met. Eng.*, 1923, 29, 184; *J.*, 1923, 940A.

¹⁹ *Bull. Rubber Growers' Assoc.*, 1923, 5, 59; *J.*, 1923, 236A.

²⁰ *Ann. Repts.*, 1923, 7, 312.

tion, this may be completed by adding alcohol. After washing, the rubber is dried at a temperature of 70° C. and weighed.

Paper made by adding latex to the pulp²¹ is now frequently met with, and certain periodicals are regularly printed on latex-containing paper.

As a result of tests carried out at 70° C., H.P.Stevens²² states that, as evidenced by the bursting tests, the presence of latex in paper is almost entirely without influence on the ageing properties.

The effect of incorporating latex is, however, evident when the paper is submitted to the folding test. Latex paper undergoes very little change on ageing, whereas similar paper not containing latex shows a much lower folding number at the end of the ageing period.

In connexion with the use of latex, an interesting pamphlet²³ has been issued by the Rubber Growers' Association, dealing with the preservatives to be employed, the types of containers recommended, and with the relative cost of latex as against crêpe or sheet rubber. It is recommended that for satisfactory shipping, 6 oz. of 0.880 ammonia be added per gallon of undiluted latex, giving a concentration of approximately 1.3% NH₃.

There has also appeared a comprehensive paper by A. Van Rossem²⁴ dealing with the industrial applications of latex.

PREPARATION OF RAW RUBBER.

Although the agent almost universally employed on the plantation for coagulating is acetic acid, there are some estates on which sulphuric acid is regularly in use, and H. P. Stevens²⁵ has drawn attention to the danger of producing a slow-curing rubber which is thus incurred. Results of the author's previous work are quoted which clearly show that even with minimal proportions of sulphuric acid the rubber produced possesses a low rate of cure, as compared with that obtained with the aid of acetic acid; the disparity is much more marked when acids are added to the same extent in excess of the minimal proportions.

In some cases the acetic acid delivered to estates in barrels is of a dark brown colour due to the presence of traces of paraffin from the barrels. According to W. Spoon²⁶ the proportions in which it usually occurs are such that the properties of the rubber are in no way affected.

²¹ *Ann. Rep's.*, 1922, 7, 310.

²² *Bull. Rubber Growers' Assoc.*, 1923, 5, 558.

²³ "The Preservation and Shipment of Latex," Rubber Growers' Association, London.

²⁴ *Chem. Weekblad*, 1923, 20, 125.

²⁵ *Bull. Rubber Growers' Assoc.*, 1923, 5, 247.

²⁶ *Comm. Central Rubber Station, Buitenzorg*, 1923, No. 32, 1; *J.*, 1923, 728.

It is known that in the preparation of rubber on the plantation variations in the rate of drying of the coagulum may occur, and O. de Vries,²⁷ after reviewing the available data, has described further experiments indicating the extent to which this may be influenced by the method of preparation. The rate of drying is increased by keeping the freshly rolled coagulum in dilute formalin, or in 10% acetic acid. Drying is retarded by previous soaking in water, or by treatment with boiling water and keeping in the sterile water; similarly, keeping in 1% acetic acid, 5% sodium bisulphite or sulphite, or 1% caustic soda was found to decrease the rate of drying. Although coagulum from very dilute latex may dry quickly, soaking in water tends to retard drying. Micro-organisms do not contribute to the slow drying effect, neither does the hygroscopicity of the rubber, which merely influences the moisture content of the air-dry rubber. Slow drying is thought to be due not to the formation of an impervious surface layer on the coagulum but to an alteration in the structure of the whole mass.

The question of preventing mould formation on smoked sheet²⁸ still continues to claim attention, and further information proving the effectiveness of sodium silicofluoride as a preventative²⁹ has been furnished by J. Edwards³⁰ and H. P. Stevens.^{31, 32} The best results are obtained by coagulating with sodium silicofluoride and then soaking the rolled coagulum in a solution of the salt.

Compared with coagulation with acetic acid, the use of sodium silicofluoride results in a slight retardation of the vulcanisation, and a further retardation is caused by the soaking of the sheet after coagulation. It is stated that even with increasing proportions of the sodium silicofluoride this effect is not sufficiently marked to constitute a disadvantage in pure or compounded mixings. The ageing properties of the vulcanised rubber are not affected harmfully.³³

Not only the sodium salt, but lead, zinc, and magnesium salts of hydrofluosilicic acid, and even the acid itself, have been found to possess the property of preventing mould formation.³⁴ Moreover, sodium, ammonium, or potassium bifluorides have been found to act in the same manner. The use of sodium silicofluoride is, in the meantime, not being recommended until tests which are now being

²⁷ Comm. Central Rubber Station, Buitenzorg, No. 32, 7; J., 1923, 732A.

²⁸ Ann. Repts., 1922, 7, 313.

²⁹ Ibid., 1923, 7, 313.

³⁰ Bull. Rubber Growers' Assoc., 1923, 5, 21.

³¹ Ibid., 1923, 5, 296; J., 1923, 667A.

³² Ibid., 1923, 5, 114, 383; J., 1923, 898A.

³³ Ibid., 1922, 5, 591, 662; J., 1923, 63A, 107A.

³⁴ H. P. Stevens, Bull. Rubber Growers' Assoc., 1923, 5, 170, 382; J., 1923, 64A, 898A.

made by three rubber manufacturers in this country are completed.³⁵

While the development of mould may give rise to slight differences in the rate of cure in simple rubber-sulphur mixings, such differences may be accentuated, as H. P. Stevens has shown,³⁶ when the rubber is compounded with litharge. The same author has brought forward additional evidence of this in the case of samples of rubber exposed to rainfall and allowed to remain in a wet condition for fifteen days.³⁷ Rubber coagulated with acetic acid and smoked was tested together with rubber coagulated with sodium silicofluoride and then soaked in a concentrated solution of the same salt before smoking. In a rubber-sulphur mixing little difference in the rate of cure was noticed, the acetic acid sample which had become covered with mould curing a little more rapidly than the sample coagulated with sodium silicofluoride which was free from mould. In a litharge mixing, however, the order was reversed, the sample coagulated with acetic acid requiring approximately twice as long for vulcanisation.

Since the advent of rubber planting on an extensive scale, the preparation of the rubber from latex has been accomplished almost exclusively by coagulating with acid.

From time to time there have been devised processes based on the evaporation of latex, as an example of which may be cited the Kerbosch method, in which the latex is delivered on to the interior surface of a heated revolving drum. These have not met with success on a commercial scale, chiefly on account of the low output from a unit plant, and also to some extent owing to the difficulties encountered in removing the film of rubber in a suitable form.

A good deal of interest has, therefore, been aroused by the Hopkinson process in which this principle is embodied, the rubber being obtained from latex by spraying into a chamber through which heated gases are led.³⁸

The latex is evaporated and the rubber therefore contains all the solids originally present, and not, as in the case of coagulated rubber, only those which are insoluble in water. The evaporation proceeds rapidly and the rubber is obtained in a form which is convenient for handling. The product obtained in this way is referred to as L.S. (i.e., latex sprayed) rubber.

In this connexion it is interesting to note that in 1911 W. Esch³⁹ suggested such a method and published a sketch of an apparatus

³⁵ *Bull. Rubber Growers' Assoc.*, 1923, 5, 525.

³⁶ *Ibid.*, 1922, 4, 520; *J.*, 1922, 989A.

³⁷ *Ibid.*, 1923, 5, 341; *J.*, 1923, 788A.

³⁸ *Ann. Repts.*, 1922, 7, 312.

³⁹ *Gummi Markt*, July, 1911; *Bull. Rubber Growers' Assoc.*, 1923, 5, 509.

suitable for the purpose, smoke being introduced together with the air employed for atomising the latex.

In recent years liquids such as milk have been desiccated by spraying into a hot atmosphere, and various types of atomisers have been devised.⁴⁰

In the Hopkinson method the latex, contained in a vessel provided with a stirrer, is delivered on to a rapidly rotating disc situated at the top of a chamber through which hot gases, as, for example, flue gases, are passed. The rubber formed by evaporation of the latex falls to the floor of the chamber as a spongy mass which, for purposes of transport, may be compressed into a compact block.⁴¹

The specific claim covered by the Hopkinson patent is a crude rubber or rubber substance obtained by evaporating latex or a porous or spongy mass of particles of rubber formed by removing moisture from latex, such dried rubber containing substantially all the solid contents of the original latex. The rubber may, if desired, be mixed with a vulcanising agent or a compounding ingredient.

The proposal has given rise to a considerable amount of discussion as to the merits and demerits of rubber containing all the serum substances, sometimes referred to as "whole" rubber.

O. de Vries⁴² points out that rubber prepared by the Kerbosch process is generally hygroscopic and, owing to the high content of serum substances, liable to become mouldy. The rate of cure is generally high and the tensile strength approximately the same as, but sometimes lower than, that prepared by a process of coagulation. The rubber crumbles on the mill and does not become plastic so readily as does normally prepared rubber; consequently, the power consumed in the milling operations is high. The rubber does not preserve its original properties on keeping so well as does ordinary plantation rubber, becoming tacky and weak in the course of four or five years, and showing signs of deterioration in a much shorter period.

The properties of rubber prepared by a spraying process have been examined by H. P. Stevens, whose results are substantially in agreement with those obtained with Kerbosch evaporated rubber. For example, the sprayed rubber has been shown to be resistant to milling; in an experiment on a factory scale it was found that whereas a normal sample of plantation sheet required 20 minutes for mastication, Hopkinson sprayed rubber required 40 minutes under the same conditions of temperature, size of batch, etc. Compounding ingredients exhibit a greater tendency to cake when being added, and, moreover, the rubber is prone to adhere to the back roller during milling. Even after thorough

⁴⁰ E.g., R. Stauf, E.P. 14,724 of 1900; G. A. Krause, E.P. 22,507 of 1913.

⁴¹ *India Rubber J.*, 1923, 65, 89.

⁴² *India Rubber J.*, 1923, 66, 101; *J.*, 1923, 842A.

milling, the plasticity of the rubber appears to be unsatisfactory, since joins or overlaps in wrapped goods are not eliminated during vulcanisation but are apparent in the vulcanised sample.⁴³

Hopkinson sprayed rubber generally vulcanises faster than normally prepared smoked sheet or crêpe, and H. P. Stevens has shown⁴⁴ that exhaustive extraction with water for a period of three weeks results in a lowering of the rate of cure. A particular sample washed in this way lost weight to the extent of 9.9%, but in an experiment⁴⁵ in which the extraction was not so prolonged, lasting only a few days, the rate of cure was not affected. In this case, however, the amount removed was 7.5%, so that 2.4% of water-soluble matter still remained in the rubber. It is worthy of note that the additional serum substances present in evaporated rubber do not increase the activity of litharge.⁴⁶

H. P. Stevens⁴⁷ has shown that the tensile strength after vulcanisation is generally lower in the case of evaporated rubber, including that obtained by spraying, although in one instance values slightly higher than the normal were obtained.⁴⁸ The retained serum solids are said to act merely as diluents and softeners, and consequently rubber vulcanised to give a standard extensibility will generally be found to be over-cured. Extraction of the water-soluble constituents before vulcanising results in the production of vulcanisates with improved tensile properties.⁴⁹

Thus, it will be seen that the production of rubber by an evaporative process, such as spraying, will possess certain advantages as, for example, the increased yield of rubber, such increase being due to the inclusion with the rubber of certain substances which may have a detrimental effect on the tensile properties. The increase in yield of rubber obtained from different samples of latex by evaporation over that obtained by coagulation was found by H. P. Stevens to vary from 8 to 17%.⁵⁰

A further claim on behalf of the adoption of the spraying process is that compounding ingredients may be added to the latex by the manufacturer, and it has been assumed that this will lead to a decrease in power consumption owing to the reduction of the period of milling necessary for the introduction of compounding ingredients to ordinary coagulated rubber. If, however, as has been indicated above, the rubber itself requires longer mastication, it would seem that the advantage to be gained on this ground is problematical.

⁴³ Bull. Rubber Growers' Assoc., 1923, 5, 446, 509; J., 1923, 988A, 1082A.

⁴⁴ *Ibid.*, 168; J., 1923, 484A.

⁴⁵ *Ibid.*, 560; *Abs.*, 1924, B, 24.

⁴⁶ H. P. Stevens, *ibid.*, 226; J., 1923, 565A.

⁴⁷ *Ibid.*, 41; J., 1923, 236A.

⁴⁸ *Ibid.*, 224; J., 1923, 865A.

⁴⁹ *Ibid.*, 561; *Abs.*, 1924, B, 24.

⁵⁰ *Ibid.*, 41; J., 1923, 236A.

Incorporation of compounding ingredients would doubtless be best accomplished by manufacturers who were prepared to instal the spraying apparatus in their works and add the necessary compounding ingredients to latex imported for the purpose. According to H. P. Stevens⁵¹ there is no reason why compounding ingredients should not be added to latex prior to coagulation in the ordinary manner, as practised on the plantations, although it is doubtful whether manufacturers would be prepared to purchase rubber already compounded in this manner.

The comparatively high power consumption of sprayed rubber during milling is confirmed by E. Hopkinson,⁵² who states that the difference in its behaviour from that of ordinary coagulated rubber is not so marked in the material now being produced in bulk as in that obtained during the earlier experimental trials. Figures quoted by Hopkinson indicate a markedly superior tensile strength for sprayed rubber as compared with plantation or fine hard Para when vulcanised with 10% of sulphur at 141° C. The ageing properties of the vulcanisates are shown to be of a very high order, and this is particularly evident when comparing over-cured samples.

CHEMICAL PROPERTIES AND CONSTITUTION.

From the results of analyses of specially purified samples of rubber, which have been carried out from time to time, the empirical formula C_6H_8 has been assigned to the caoutchouc hydrocarbon, and at present this finds almost universal acceptance.

Recently, however, F. Kirchhof⁵³ has sought to show that the empirical formula of the caoutchouc hydrocarbon present in Para rubber is $C_{10}H_{17}$, the molecular formula being $C_{20}H_{34}$. The approximation of previous analyses to this formula will be seen by comparing the figures obtained by C. Harries⁵⁴ with those calculated for $C_{10}H_{16}$ and $C_{10}H_{17}$ respectively,

| | | C. | H. |
|----------------|-------|--------|--------|
| $C_{10}H_{16}$ | | 88.15% | 11.85% |
| $C_{10}H_{17}$ | | 87.51 | 12.49 |
| Harries | | 87.85 | 12.28 |

It will be observed that the figures obtained by Harries are almost intermediate between those calculated for the two empirical formulæ.

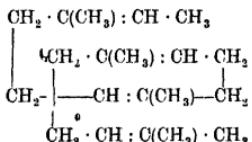
Kirchhof proposes an open-chain spiral structure for the caoutchouc hydrocarbon,

⁵¹ H. P. Stevens, *ibid.*, 1923, 5, 48.

⁵² *Ind. Eng. Chem.*, 1923, 15, 1267.

⁵³ *Oesterr. Chem.-Zeit.*, 1922, 25, 143, 150; *J.*, 1923, 23A.

⁵⁴ "Untersuchungen über die natürlichen und künstlichen Kautschukarten," Berlin, 1919, p. 7.



which has some points of similarity to that propounded by F. Barrow⁵⁵ some time back. Kirchhof assumes that the caoutchouc present in Para rubber differs chemically from that present in other grades, such as Congo rubber, which he supposes to contain a hydrocarbon $\text{C}_{10}\text{H}_{16}$. There is no doubt that the empirical formula C_5H_8 has been accepted hitherto without question chiefly on account of the supposed identity of the product of polymerisation of isoprene with natural caoutchouc. The fact that analyses are sometimes obtained which are not strictly in accordance with the generally accepted formula has usually been attributed to the presence of traces of accessory substances retained even after a process of purification.

In an important paper, R. Pummerer and P. A. Burkard⁵⁶ have dealt with the question of the empirical formula, and their evidence is in support of the C_5H_8 ratio. The rubber they employed was purified by the method of Harries, but the precaution was taken to carry out the operations in an atmosphere of carbon dioxide so as to prevent oxidation taking place. Analysis gave $\text{C} = 87.96\%$, $\text{H} = 11.82\%$, which is in fairly close agreement with the calculated proportions. Further evidence in support of the C_5H_8 ratio was afforded by the results they obtained on hydrogenating purified caoutchouc. Staudinger and Fritsch,⁵⁷ who also succeeded in hydrogenating caoutchouc, employed temperatures as high as 270° C ., under which conditions caoutchouc itself is not stable. Pummerer and Burkard, however, succeeded in effecting hydrogenation at comparatively low temperatures. The purified rubber was dissolved in hexahydrotoluene, platinum black being employed as a catalyst. The best results were obtained by working with dilute solutions (0.2-0.6%) at temperatures of 70° - 80° C ., when absorption of hydrogen took place, and was complete in 3 hours; with solutions of 1% concentration absorption of hydrogen was not complete. The absorption of hydrogen was determined volumetrically, and in all cases the amount taken up corresponded very closely with that theoretically required for the addition of two atoms of hydrogen for each C_5H_8 . The hydrocaoutchouc was obtained by precipitating the platinum black with the aid of kaolin and, after separating the clear supernatant

⁵⁵ *India Rubber J.*, 1911, 41, 1354.

⁵⁶ *Ber.*, 1922, 55, 3458; *J.*, 1923, 23A.

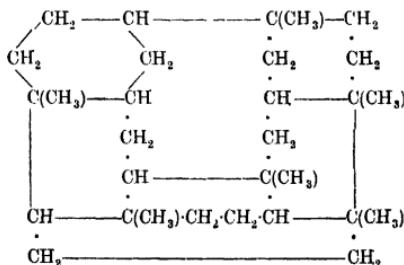
⁵⁷ *Ann. Repts.*, 1922, 7, 315.

liquor, evaporating this to dryness in absence of oxygen, when a transparent elastic film was obtained, giving on analysis figures corresponding with the empirical formula CH_2 , i.e., C_5H_{10} .

It is of interest to note that this hydrocaoutchouc is readily oxidised on exposure to air with the reproduction of a hydrocarbon C_5H_8 closely akin to the original caoutchouc; this indicates that the added hydrogen atoms are in a loose state of combination compared with the remainder.

Pummerer and Burkard conclude that the structure of the caoutchouc molecule is represented either by a ring or by an extremely long open chain, in which case the formula $\text{C}_{5x}\text{H}_{8x}$ approximates to $\text{C}_{5x}\text{H}_{8x+2}$.

From a consideration of the work of previous investigators and as a result of further experiments carried out by himself and his collaborators, M. C. Boswell⁵⁸ has propounded a constitutional formula for caoutchouc which differs entirely from any which has been hitherto put forward. According to Boswell, none of the previous formulae has explained the formation of terpenic compounds such as dipentene, on destructive distillation, and dinitro-hydrocumic acid on treatment with nitric acid.⁵⁹ The proposed structural formula is as follows:—



An examination will show that this is made up of six isoprene residues, giving a formula $\text{C}_{30}\text{H}_{48}$ for the caoutchouc molecule. Decomposition might be expected to yield, among other substances, dipentene, although not more than one molecular proportion, or 33½% by weight of the whole. One dimethyl-cyclo-octadiene residue is present which would explain the formation of the ozonide, assuming that fission of the system took place at ordinary temperatures in presence of ozone. The proportion of ozonide formed would thus be comparatively small, and Boswell points out that this is in agreement with the results of Olivier,⁶⁰

⁵⁸ *India Rubber J.*, 1922, **64**, 983; *J.*, 1923, 63A.

⁵⁹ *Ditmar, J.*, 1904, 794.

⁶⁰ *Rec. Trav. Chim.*, 1921, **40**, 665.

who was unable to obtain yields of ozonide corresponding to the conversion of the whole of the caoutchouc taken, such as would be expected from a compound of the structure usually assigned to caoutchouc, that is, a single ring composed of isoprene nuclei linked together directly.

The unsaturated nature of caoutchouc is not, however, indicated in the formula, and Boswell assumes that the action of bromine, for example, is first of all to effect depolymerisation of the molecule, addition of bromine then taking place.

The experiments of Pummerer and Burkard on the hydrogenation of caoutchouc have emphasised the unsaturated character of the molecule, and it is difficult to understand how a structure such as that represented by Boswell is to split up into unsaturated units capable of forming addition compounds of high molecular weight such as the derivatives of caoutchouc undoubtedly are. One would further expect to obtain a variety of compounds by different treatments. Destructive distillation, for example, should furnish a much wider range of products than are obtained from rubber, and similarly on bromination one would expect to obtain a mixture containing substances of comparatively simple structure.

The action of chlorine on caoutchouc has been investigated by J. McGavack,⁶¹ who has sought to determine the extent to which substitution and addition take place simultaneously. Previous workers have found that while the reaction with bromine may be controlled so as to avoid substitution, during the reaction with chlorine substitution takes place with evolution of hydrogen chloride and a comparatively highly chlorinated substance is formed, even in an ice-cooled benzene solution. Hinrichsen, Memmler, and Kindscher⁶² obtained a compound $C_{10}H_{14}Cl_6$, indicating the addition of 4 atoms of chlorine and the substitution of three further atoms for each $C_{10}H_{16}$ residue. McGavack's results indicated that in the earlier part of the reaction substitution occurred almost exclusively, but that as the reaction proceeded, addition of chlorine began to take place, the proportion of hydrogen chloride formed being thus reduced.

Iodine has been frequently stated to be without action on caoutchouc, although in presence of air an oxygenated compound containing iodine was obtained by Schwartz and Kempff.⁶³ M. C. Boswell, R. R. McLaughlin, and R. R. Parker⁶⁴ have obtained a somewhat similar product from the interaction in the cold for two

⁶¹ *Ind. Eng. Chem.*, 1923, 15, 961; *J.*, 1923, 1033A.

⁶² *Ber.*, 1913, 46, 1283.

⁶³ *Ber.*, 1913, 46, 1287.

⁶⁴ *Loc. cit.*

weeks of iodine, hydrogen peroxide, and caoutchouc in carbon tetrachloride solution. By extracting the reaction product with ethyl acetate a brownish yellow powder was obtained, the analysis of which corresponded to the composition $C_{25}H_{40}O_8I$.

The same authors have also investigated the action of oxidising agents, including atmospheric oxygen. Thin sheets of resin-free rubber were exposed to the air in direct sunlight for three months, at the end of which time approximately 30% of the rubber was converted into acetone-soluble substances. A proportion of the oxidation product was soluble in carbon disulphide, and after purification gave, on analysis, figures corresponding to the formula $C_{10}H_{16}O$. It is interesting to note that Pummerer and Burkard⁶⁵ by determining the volume of oxygen absorbed by a solution of rubber in hexahydrotoluene, either in presence or absence of platinum black, found that oxygen was taken up in proportion corresponding with the formation of a compound of this formula. The compound insoluble in carbon bisulphide, without further purification, gave on analysis figures agreeing with the composition $C_{25}H_{40}O_8$.

The action of hydrogen peroxide on rubber was also studied by shaking a solution of rubber in carbon tetrachloride with a 3% solution of hydrogen peroxide for one week, at ordinary temperatures. The aqueous portion of the reaction mixture gave on evaporation a sticky mass which absorbed oxygen rapidly, but this was not fully investigated. The carbon tetrachloride solution gave a transparent bright yellow substance, partially soluble in ether, from which solution there was obtained by further purification a substance of the composition $C_{30}H_{48}O$, which, on exposure to air, absorbed oxygen with formation of a compound $C_{25}H_{40}O_2$, thus indicating the simultaneous elimination of an isoprene nucleus C_5H_8 .

M. C. Boswell and A. Hambleton⁶⁶ also investigated the action of an aqueous solution of potassium permanganate on rubber dissolved in carbon tetrachloride, but it was difficult to isolate from the reaction mixture a substance having a constant composition, although the analyses were in fair agreement with the empirical formula $C_{25}H_{40}O$. This substance on standing in the air at ordinary temperatures rapidly took up oxygen with formation of a compound $C_{25}H_{40}O_2$.

The destructive distillation of rubber has long been known to result in the formation of a liquid containing a high proportion of dipentene, and, indeed, the distillation of rubber for the production of commercially valuable solvents was practised in the early part

⁶⁵ Loc. cit.

⁶⁶ Loc. cit.

of last century. A. Van Rossem and P. Dekker⁶⁷ have examined the products of dry distillation of scrap rubber, which were found to yield 50% of a fraction boiling below 200° C. It is suggested that this might be useful as a substitute for turpentine, and in this way scrap rubber produced on plantations, which could not be otherwise utilised, could be turned to good account. This suggestion affords a rather curious instance of inversion of economic values, since it is only a few years ago that turpentine was considered as a likely starting point for the production of synthetic rubber, and now natural rubber is being considered as a source of a turpentine-like product.

In a similar manner C. Lefebvre⁶⁸ proposes to obtain an oil having the properties of oil of turpentine by the destructive distillation of waste vulcanised rubber.

The action of selenium oxychloride on purified caoutchouc⁶⁹ prepared from different grades of natural rubber and on synthetic rubber prepared from isoprene, in carbon tetrachloride solution, has been studied by C. E. Frick.⁷⁰ It was not found possible to effect complete purification of the products (which contained selenium and chlorine), but the author concludes from the analytical results obtained that there is no difference in empirical composition between the pure rubber obtained from a typical natural rubber and the synthetic product obtained by the polymerisation of isoprene.

PHYSICAL PROPERTIES.

While the physical properties of raw rubber have not been studied so intensively as those of vulcanised rubber, a good deal of attention has been devoted to the solution viscosity, particularly with respect to the possibility of correlating this property with that of the rubber after vulcanisation, although such correlation has been shown not to be generally applicable.

It has been known for some time that the viscosity of rubber solutions is reduced considerably by the addition of traces of acids, such as trichloroacetic acid, and this phenomenon has been made the basis of a method for isolating the insoluble nitrogenous constituent present in a solution from which it would otherwise settle out only with difficulty.

The effect of adding other reagents such as benzoic acid, acetic acid, mercuric chloride, and sulphurous acid, has been studied by W. A. N. Eggink,⁷¹ who finds that in each case a decrease in viscosity occurs. On the other hand, addition of ammonia causes an

⁶⁷ *Chem. Weekblad*, 1923, **20**, 78; *J.*, 1923, 280A.

⁶⁸ E.P. 188,008; *J.*, 1923, 23A.

⁶⁹ Cf. V. Lenher, *J. Amer. Chem. Soc.*, 1921, **43**, 29.

⁷⁰ *Ibid.*, 1923, **45**, 1800; *J.*, 1923, 844A.

⁷¹ *Rec. Trav. Chim.*, 1923, **42**, 317; *J.*, 1923, 510A.

increase of viscosity. The decrease in viscosity brought about by adding an electrolyte is attributed to the removal of the electrical charge, and the author suggests that if such a procedure were adopted before carrying out viscosity determinations, any relationship between viscosity and vulcanising properties, which otherwise would be obscured, might become more apparent.

In a series of experiments carried out with dilute (0·03–0·47%) solutions of rubber in benzene, K. Shimida⁷² finds that the viscosity-concentration relationship is in accordance with Arrhenius' formula $\log \eta/\eta_0 = \theta C$, where η is the viscosity of the solution, η_0 that of the solvent, and C the concentration of rubber in the solution. The results are not affected by the presence of resin associated with the rubber.

The swelling of raw rubber in organic liquids has been investigated by M. Le Blanc and M. Kroger,⁷³ who find that the degree of maximum swelling increases with increasing dielectric constant, a result which is not in agreement with the view of Wo. Ostwald,⁷⁴ who concluded, from an examination of the results of other workers, that the swelling power decreased with increasing dielectric constant of the swelling liquid. According to Le Blanc and Kroger, compounds containing halogen or sulphur exhibit the greatest maximum swelling power. At the commencement of the swelling action the velocity of swelling depends to a large extent upon the viscosity of the liquid, and on this account a liquid producing maximum swelling of a comparatively low order may have a swelling velocity considerably higher than one which produces a greater maximum swelling. The effectiveness of carbon bisulphide as a solvent for sulphur chloride in cold vulcanisation is attributed to its unusually high swelling velocity.

VULCANISATION.

The results of a very comprehensive series of researches on the mechanism of the cold and hot vulcanisation processes, carried out by B. V. Bysow and M. K. Popova,⁷⁵ are now available, and in many respects supplement and confirm previous work of the first-named author. Much of the work covers ground already traversed by other workers, and it may be that the experiments were in progress at a time when information regarding these was not available.

Vulcanisation with the aid of sulphur chloride is said to be an adsorptive process, although in certain solvents, such as ether, benzene, and chloroform, characteristic adsorption curves were not

⁷² *J. Chem. Ind., Japan*, 1923, **26**, 705; *J.*, 1923, 788A.

⁷³ *Kolloid-Zeits.*, 1923, **33**, 168; *J.*, 1923, 1082A.

⁷⁴ *Ibid.*, 1921, **29**, 100; *J.*, 1921, 667A.

⁷⁵ *J. Russ. Phys.-Chem. Soc.*, 1921, **53**, 20-180; *J.*, 1923, 842A.

obtained, this being attributed to the occurrence of side-reactions with the solvents.

Rubber vulcanised with sulphur chloride, after soaking in benzene, followed by extraction for three days with boiling acetone, lost about two-thirds of the sulphur chloride, chlorine being removed in greater proportion than sulphur, although it is stated that there were indications that a reaction had occurred with some of the solvent used, as the increase in weight of the rubber after vulcanisation was greater than that calculated from the added chlorine and sulphur. Vulcanisation with sulphur monobromide was found to take place in a manner similar to that with sulphur chloride. The authors also investigated the effect of immersing at ordinary temperatures raw rubber in solutions of sulphur in a solvent consisting of a mixture of 75% benzene and 25% sulphur chloride. It is stated that the amount of sulphur taken up was dependent on the concentration, and indicated an adsorption process.

It was found that water vapour had an accelerating influence on the progress of hot vulcanisation. It is stated that in hot vulcanisation rubber first adsorbs melted sulphur,⁷⁶ part of which remains in a super-cooled condition, insoluble in acetone, another part crystallising out on cooling, and a third part combining chemically with the rubber. The sulphur in vulcanised rubber is therefore present in three states: crystalline sulphur soluble in acetone, amorphous super-cooled sulphur which is insoluble in acetone but which may be oxidised by means of bromine water, and thirdly, chemically combined sulphur which is both insoluble in acetone and not oxidisable by bromine water.

The effect of solvents on rubber vulcanised to different degrees was examined, and results were obtained which were generally in accordance with those of Stevens.⁷⁷

The heat of combustion of vulcanised rubber was found to be the same as that of unvulcanised rubber, containing the same proportion of sulphur. On heating at temperatures above 155° C. mixtures containing over 30% of sulphur, however, gave an exothermic reaction accompanied by the evolution of some hydrogen sulphide. Somewhat similar observations have been made by I. Williams and D. J. Beaver⁷⁸ in experiments on the vulcanising of small samples of rubber and sulphur at various temperatures. Up to 151° C. the temperature of the interior of the mixing did not rise above that of the source of heat, but at 161°, 172°, and 176° C. the temperature rose to 163°, 178°, and 203° C. respectively. With increasing proportions of sulphur up to 14%, or with the

⁷⁶ Cf. D. Spence, *Kolloid-Zeits.*, 1911, **9**, 300.

⁷⁷ *Ann. Repts.*, 1919, **4**, 340.

⁷⁸ *Ind. Eng. Chem.*, 1923, **15**, 255; *J.*, 1923, 412A.

ntroduction of an organic accelerator an increased temperature rise occurred. When mixtures of sulphur and resin, or of sulphur and accelerator were heated separately, the temperature rise was very small.

Acetone-extracted rubber, when vulcanised, gave a much lower temperature rise than the unextracted, due to the extreme slowness of the reaction, whereby the heat evolved tends to be dissipated. Although the temperature rise seems to indicate quite large energy changes during vulcanisation, heats of combustion show that in reality these are comparatively small. Rubber containing 6.5% sulphur was vulcanised to give on the one hand 0.7%, and on the other hand 5.6% of combined sulphur, and the heats of combustion were 5819 and 5832 calories per gram respectively. Further experiments tended to show that during vulcanisation both an exothermic and an endothermic reaction took place, the latter predominating only towards the end of the reaction.

An interesting development in the technique of vulcanisation is the discovery of P. Schidrowitz that rubber in the latex form can be vulcanised without coagulation occurring.⁷⁹ This vulcanised latex can then be employed for the purpose of proofing fabrics, giving a rubber coating which is already vulcanised. Alternatively, the latex may be coagulated to give a vulcanised rubber mass.

Experiments on the vulcanisation of latex are described by W. C. Davey,⁸⁰ and it is interesting to note that there are several respects in which the vulcanisation differs from that of ordinary rubber. The general procedure consists in mixing the sulphur to a thick cream with ammonia, adding this to the previously strained latex, and heating in an autoclave, giving a rise of 10 minutes to the vulcanising temperature, in most cases 141° C. At the end of the heating period the steam is allowed to blow off very slowly. Owing to the escape of ammonia during the operation, it is necessary to add a fresh quantity to prevent coagulation taking place, if the latex is to be kept.

After vulcanisation very little change is noticeable, and on microscopical examination Brownian movement is seen to persist.

For purposes of testing, the rubber may either be coagulated with acetone and converted to crêpe or evaporated spontaneously to give a thin film. Vulcanisation, as evidenced by combination of sulphur, takes place comparatively rapidly in the early stages of the heating, but then slows down. In one experiment 100 c.c. of latex, giving 33% of rubber on coagulation, was mixed with 500 c.c. of water and 2 grams of sulphur. After heating for 1 hour at 141° C. the coefficient of vulcanisation was 0.91; at the end of 2 hours this had risen to 1.07 only. The rate of combinatio-

⁷⁹ E.P. 193,451; J., 1923, 732A.

⁸⁰ J., 1923, 473T.

with sulphur varies according to the nature of the sulphur. Similar mixings of different forms of sulphur heated for the same time gave co-efficients of vulcanisation: in the case of flowers of sulphur, 0.55; precipitated sulphur, 1.47; and colloidal sulphur, 2.44. Polysulphides may also be employed for effecting vulcanisation. Increase in the proportion of sulphur brings about an increase in the rate of cure, but the relationship is not a linear one. Dilution of the latex tends to retard vulcanisation, as also does the addition of ammonia. The presence of litharge does not accelerate vulcanisation, as judged by the combined sulphur, and both lime and magnesia cause coagulation to take place during the heating.

In the presence of small proportions of zinc oxide the rate of combination of sulphur with the rubber is increased, but with larger proportions, vulcanisation is retarded. If, however, zinc oxide is introduced in the form of the hydroxide dissolved in excess of ammonia, marked acceleration results.

At temperatures of 140° C., or thereabouts, organic accelerators do not exhibit the same activity with respect to latex as to ordinary rubber, but at lower temperatures the power of acceleration is very much enhanced.

COMPOUNDING INGREDIENTS.

A good deal of work continues to be done on the specific effects of various compounding ingredients on the properties of vulcanised rubber, and, although a mass of information has been collected with reference to the tensile strengths and resilient energy of such compounded rubber, less attention has been paid to the resistance to abrasion which, in some cases, particularly that of tyres, is of considerable importance. A systematic investigation has been carried out by H. W. Greider⁵¹ for the purpose of determining the abrasion resistance of vulcanised rubber. To a basic mixing composed of rubber 100, sulphur 5, zinc oxide 5, hexamethylenetetramine 1 (parts by weight), increasing volumes of the pigment were added. From sheets of the vulcanised rubber annular test pieces were stamped out, and these were tested according to the method described by Evans (see p. 380). Of the fillers employed, both lithopone and colloidal barium sulphate, when added even in small proportion, reduced the resistance to abrasion, and further addition resulted in a progressive decrease in the resistance.

Addition of the remaining fillers in gradually increasing proportions caused at first an increase in abrasion resistance which, after reaching a maximum, steadily diminished.

The filler giving the highest maximum resistance to abrasion was "gas black," which, in the proportion of 21 vols. per 100

⁵¹ *Ind. Eng. Chem.*, 1923, 15, 504; *J.*, 1923, 615A.

vols. of rubber, gave a value of about 18 for the coefficient of abrasion resistance. Light magnesium carbonate came next with a maximum coefficient of 15, obtained with 6 vols. of filler per 100 vols. of rubber; china clay and zinc oxide both gave a maximum of about 12 at about 10 vols. of added filler. The curves obtained by plotting the resistance to abrasion against the volumes of added filler per 100 vols. of rubber were almost identical with those obtained by plotting the tensile strength in the same way. It was found that there was in general a correlation between hardness of the vulcanised rubbers as determined by the indentation test and their resistance to abrasion. The author considers that in order to obtain vulcanised rubber of a high degree of resistance to abrasion, it is necessary to use fillers which will impart rigidity, high tensile strength, and high resilient energy capacity which involves the possession of high tensile strength, together with high extensibility. As it would be difficult to secure all these conditions by the use of one filler, it is suggested that a combination of two or more fillers would give the most satisfactory results. In the author's opinion, the fillers which most nearly fulfil these conditions are light magnesium carbonate and carbon black, and the results of experiments are quoted in which these fillers were employed in the proportions 10-5, 12-6, and 14-7 vols. of gas black to magnesium carbonate per 100 vols. of rubber.

The presence of compounding ingredients frequently results in the rubber exhibiting anisotropy in its physical properties. An instance of this behaviour is afforded by the so-called calender grain, which in the absence of special precautions is usually met with even in the case of pure rubber mixings before vulcanisation. W. B. Wiegand and H. A. Braendle,²² by examining the effect of vulcanising pure and compound mixings under various conditions, have shown that the grain effect may persist even after vulcanisation, and that the extent to which it is evident depends both on the manner in which vulcanising is carried out, and upon the presence or otherwise of fillers. The difference in mechanical properties of the vulcanised samples determined with and across the grain afforded evidence of the persistence of the grain.

In the case of the "pure" rubber-sulphur mixing very little anisotropy was exhibited when the sample was subject to maximum distortion during vulcanisation or when maximum freedom of movement was allowed. On the other hand, where the movement of the sample was restricted the grain was still in evidence after vulcanisation.

In the presence of compounding ingredients, however, the grain effect remains to a greater or less extent whatever the conditions of

²² *Ind. Eng. Chem.*, 1923, **15**, 259; *J.*, 1923, 412A.

vulcanisation, but the phenomenon is more marked when the fillers are of a crystalline character.

The grain effect is, therefore, of a dual character and may be due to the rubber phase, although this may be eliminated to a considerable extent by adjusting the conditions of vulcanisation, and also to the influence of fillers, in which case it is more persistent.

Further evidence of anisotropy in mechanical properties induced by fillers is brought forward by W. W. Vogt and R. D. Evans⁸³ in a study of the dimensional changes occurring on stretching vulcanised rubber. When a test strip of a simple rubber-sulphur mixing is stretched the ratio of the thickness to the width remains constant as the elongation increases; the same phenomenon is observed with rubber compounded with certain fillers, for example, carbon blacks, zinc oxide, red iron oxide, ground natural barytes, whiting, and lithopone. On the other hand, the ratio of the thickness to the width of strips compounded with magnesium carbonate, mica, graphite, clay (presumably not "colloidal") or tripoli powder, gradually diminishes on stretching. In these cases, therefore, the values for Poisson's ratio will be different according to whether the elongation is compared with contraction in the direction of the width or of the thickness.

In the presence of fillers of the latter kind anisotropy is also observed in the volume changes which take place on stretching,⁸⁴ according to the direction in which the tension is applied. The increase in volume on stretching along the grain is least; across the grain gives a somewhat larger increase; and when stretched in a direction perpendicular to the grain the volume increase is largest of all. Fillers which cause anisotropy of the properties of the vulcanised rubber are termed anisotropic in contradistinction to those which give rise to the same mechanical properties when the vulcanised rubber is tested in all directions and which are termed isotropic; these terms strictly refer to the vulcanised rubber as a whole and not necessarily to the fillers. The anisotropy in properties is shown to be due to the shape of the particles of the fillers employed, those which are tabular or needle-shaped becoming oriented during calendering with their longer axes in the direction of the length of the sheet and thus the movement of the rubber varies according to whether tension is applied perpendicularly to the longer or shorter dimensions.

The influence of particle size on the properties of compounding ingredients has been emphasised in previous reports, and further evidence has been furnished by D. F. Twiss⁸⁵ in the course of a very comprehensive survey of the various fillers employed in

⁸³ *Ind. Eng. Chem.*, 1923, 15, 1015; *J.*, 1923, 1186A.

⁸⁴ *Ann. Repts.*, 1922, 7, 321.

⁸⁵ *India Rubber J.*, 1923, 65, 694; *J.*, 1923, 615A.

rubber manufacture. It is shown that calcined magnesia is more active as an accelerator when prepared by heating light magnesium carbonate than when prepared by igniting heavy magnesium carbonate in which the particles are relatively large.⁸⁶ The same author shows that differences may result from the use of fillers occurring in different crystalline forms; litharge, for example occurs in the brown and yellow modifications which have been the subjects of investigation by M. P. Applebey and R. D. Reid,⁸⁷ who have proved that the yellow variety is the less stable, and consequently the more soluble of the two. Experiments by Twiss show that the yellow variety is more active as an accelerator, and this is attributed to its being more readily soluble in the rubber, or more probably, in the rubber resins.⁸⁸

The method of preparation of a pigment or filler can frequently be regulated so that the particles are of suitable dimensions. In the case of zinc oxide, it is stated that if metallic zinc is heated and the vapour which distils superheated to about 2000° C., and then passed into a suitable duct in contact with large excess of air rapid oxidation and cooling are effected, and in this way it is possible to prepare the pigment so that the maximum particle size is 0.25 micron.⁸⁹

Methods for determining the particle size of pigments have been referred to in previous reports. The one described by W. W. Vogt,⁹⁰ consisting in dispersing the pigment in a suitable medium and finding the height of a column necessary to obscure a given source of light, has been criticised by E. B. Spear and H. A. Endres,⁹¹ who, as the result of numerous experiments, conclude that the method is applicable for comparisons of particle size of different samples of the same pigment, if the average diameter of the particle is greater than one half the wave length of light. The method, however, is not satisfactory when applied to the comparison of different pigments possessing different optical properties such as refractive index, light absorption, etc.⁹²

An interesting method has been proposed by F. v. Hahn and D. Hahn,⁹³ employing an apparatus based upon one employed by Wo. Ostwald and F. v. Hahn⁹⁴ for the measurement of coagulation in colloidal suspensions. The method is based upon the measurement of the rate of sedimentation of pigment when suspended in a

⁸⁶ Cf. H. P. Stevens, *India Rubber J.*, 1919, **58**, 527.

⁸⁷ *Chem. Soc. Trans.*, 1922, **121**, 2129; *J.*, 1922, 980A.

⁸⁸ Cf. G. S. Whitby and A. Cambron, *J.*, 1923, 333T.

⁸⁹ New Jersey Zinc Co. and others, E.P. 180,080. *J.*, 1923, 1020A.

⁹⁰ *Ann. Repts.*, 1922, **7**, 319.

⁹¹ *Ind. Eng. Chem.*, 1923, **15**, 725; *J.*, 1923, 841A.

⁹² Cf. W. Feldenheimer, *Rubber Age*, 1922, **3**, 8.

⁹³ *Kolloid-Zeits.*, 1922, **31**, 96; *J.*, 1922, 839A.

⁹⁴ *Ibid.*, 1922, **30**, 62; *J.*, 1922, 839A.

liquid medium, as indicated by the change in specific gravity of the liquid containing the filler in suspension as sedimentation proceeds.

The microscopical examination of pigments has been dealt with by H. Green,⁹⁵ who points out that in the interpretation of photomicrographs errors are likely to arise owing to working with inadequate resolving power. The tendency of most pigments to flocculate leads to confusion between individual particles and aggregates.

For the preparation of sections for microscopical examination A. F. Hardman⁹⁶ recommends immersing the sample in molten sulphur which causes further vulcanisation and consequent hardening to occur. In this condition the sample may be cut readily. The method has been applied to the examination of rubber containing antimony sulphide, for which it is particularly suitable.

In vulcanised rubber which is subjected to continual wear for long periods, as, for example, in the treads of tyres, heat development may occur, and if this is not dissipated comparatively quickly the temperature of the rubber may rise to such an extent that rapid deterioration will take place. It is important, therefore, that the compounding ingredients should possess sufficiently high thermal conductivity to prevent heating up.

Methods for determining the conductivity of rubber mixings compounded with different fillers have been described by I. Williams.⁹⁷ In one case, the compounded rubber is applied to the outside of a cylindrical vessel made of copper through which steam may be passed. A specially constructed water trap is provided in order to keep back water which might enter with the steam, and the weight of water condensed within the vessel over a given time is ascertained. During the operation the vessel is immersed in a bath of water and the temperature rise of the bath is noted.

The second method consists in rolling the calendered rubber round a thermocouple so that it forms a cylinder $\frac{3}{4}$ -in. in diameter, in the centre of which the thermocouple is disposed. The whole is wrapped in aluminium foil and immersed in boiling water, and the temperature recorded by the thermocouple noted at intervals.

The first method gives the more accurate results, but the second is said to give results sufficiently accurate for most purposes.

The thermal conductivity of a range of pigments was determined, the highest value being obtained with zinc oxide, red iron oxide being next; the conductivity of sulphur was lowest, the values for antimony sulphide, rubber itself, litharge, clay, talc, and gas black ascending in the order given.

⁹⁵ *Chem. and Met. Eng.*, 1923, **28**, 53; *J.*, 1923, 277A.

⁹⁶ *India Rubber World*, 1923, **68**, 711.

⁹⁷ *Ind. Eng. Chem.*, 1923, **15**, 154; *J.*, 1923, 279A.

The temperature development in tyre treads incorporated with different fillers has been studied by D. F. Cranor.⁹⁸ A tyre was built up in which the tread was in four sections in which the different compounding ingredients used were zinc oxide, carbon black, glue, and clay respectively. Temperatures were taken by means of a thermocouple under normal running conditions, and it was found that the least temperature rise occurred in the portion of the tread containing zinc oxide. The portion containing clay became only slightly warmer, glue came next in order, and carbon black showed the greatest temperature rise. Tests carried out on a laboratory machine gave somewhat similar results, although it was noticed that in some cases the clay compound showed the least temperature rise.

An interesting application of selenium as a compounding ingredient is suggested by I. Williams,⁹⁹ who finds that the presence of a very small proportion, less than 0·1%, is sufficient to prevent supersaturation of the rubber with sulphur, and thus blooming is prevented.

INORGANIC ACCELERATORS.

The accelerating effect of arsenic sulphide, which has long been used as a pigment in the rubber industry, has been determined by D. F. Twiss.¹⁰⁰ With 5% of the pigment in a rubber-sulphur (90 : 10) mixing there was a reduction in time of cure at 148° C., and even in much smaller proportions B. J. Eaton and R. O. Bishop¹⁰¹ have found that marked acceleration occurs.

Experiments carried out by these authors with mixings containing arsenious oxide show that the addition in very small proportions (as little as 0·1% calculated on the whole mixing) causes acceleration, but that larger quantities do not produce a correspondingly higher degree of acceleration. This observation is of some technical interest in view of the possibility of arsenic being present in small proportion in commercial sulphur, a circumstance which might lead to errors in vulcanisation. That antimony sulphide may function as an accelerator has been shown by E. Anderson and W. M. Ames,¹⁰² but this may possibly be due to the substance containing a sulphide of antimony higher than the trisulphide, as it has already been established that polysulphides generally act as accelerators.¹⁰³ These authors also confirm the statement of A. H. King¹⁰⁴ that iron oxide in presence of brown rubber substitute acts as an accelerator.

⁹⁸ *India Rubber World*, 1923, **68**, 429.

⁹⁹ *Ind. Eng. Chem.*, 1923, **15**, 1019; *J.*, 1923, 412A.

¹⁰⁰ *India Rubber J.*, 1923, **65**, 696; *J.*, 1923, 615A.

¹⁰¹ *J.*, 1923, 303T.

¹⁰² *J.*, 1923, 138T.

¹⁰³ C. W. Bedford and L. B. Sebrell, *Ann. Repts.*, 1922, **7**, 316.

¹⁰⁴ *India Rubber J.*, 1916, **52**, 439.

The accelerating influence of ammonia has been known for some time, and in this connexion it is interesting to note that metallic ammines, such as the addition product of ammonia with zinc sulphate, $ZnSO_4 \cdot 5NH_3$, possess marked accelerating properties,¹⁰⁵ a compound of this type having recently been put upon the market.

ORGANIC ACCELERATORS.

Recent work on organic accelerators is concerned not so much with the discovery of new individual substances or classes of substances capable of acting as accelerators as with the determination of conditions of vulcanisation under which particular accelerators may be used to the best advantage.

The only important new class of accelerator described is that of the dithio-acids containing the grouping -CS-SH. Dithiocarbamates have been recognised as active accelerators for some time, but the activity was originally regarded as a function of the amino grouping. It is probable that the active group in this class of accelerators is really the -C(: S)-S- group, as S. M. Cadwell,¹⁰⁶ E. Romani,¹⁰⁷ and G. Bruni¹⁰⁸ find that the dithio-acids which do not contain the amino group are "ultra-accelerators" in presence of zinc oxide. The dithio-acids are prepared by treating the corresponding aldehydes with hydrogen persulphide or, preferably by the action of ammonium polysulphide on an alcoholic solution of the aldehydes. Thus, furfural yields dithiopyromucic acid, salicylaldehyde gives dithiosalicylic acid, and dithiobenzoic acid is obtained from benzaldehyde.

An investigation on the activities of various derivatives of 1-mercaptopbenzothiazole has been carried out by L. B. Sebrell and C. E. Boord.¹⁰⁹ The compounds used were prepared by four different methods,¹¹⁰ which consisted in heating in a steel autoclave mixtures of (1) substituted dithioureas with sulphur, according to the method of E. Romani,¹¹¹ (2) zinc salt of the corresponding aryl dithiocarbamic acid and sulphur, (3) the ammonium salt of the same acid and sulphur, (4) the arylamine, carbon disulphide, and sulphur.

The properties of the thiazoles, their lead and zinc salts, and their disulphides are described in detail. In the compounds prepared by the authors various substituent groups were introduced into the benzene nucleus, and the activities as accelerators of these

¹⁰⁵ H. Skellon, T. H. Roberts, and H. B. R. Clarke, E.P. 204,902; *J.*, 1922, 1187A.

¹⁰⁶ E.P. 177,493; *J.*, 1923, 1033A.

¹⁰⁷ *Caoutchouc et Gutta Percha*, 1922, 18, 11,626; *J.*, 1923, 107A.

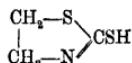
¹⁰⁸ *India Rubber J.*, 1922, 64, 927; *J.*, 1923, 63A.

¹⁰⁹ *Ind. Eng. Chem.*, 1923, 15, 1009; *J.*, 1923, 1187A.

¹¹⁰ *J. Amer. Chem. Soc.*, 1923, 45, 2390.

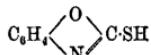
¹¹¹ *Gaz. Chim. Ital.*, 1922, 52, 29.

derivatives determined in a mixing, rubber 100, sulphur 3·5, zinc oxide 5, together with 1 part of 1-mercaptopbenzothiazole or the molecular equivalent of the substituted compound. Temperatures of 125° and 141° C. were employed, and the compounds ranged in order of activity as determined by the load necessary to give an elongation of 700% at 10 minutes cure. The most active substance was found to be 1-mercaptop-3-methylbenzothiazole, the order of the remainder being as follows:—3,5-dimethyl, parent substance, 5-methyl, 5-ethoxy, 5-methoxy. The accelerators were in the same order at both temperatures. In the absence of zinc oxide the acceleration produced was extremely small, and the zinc salts exhibited a similar behaviour, requiring the presence of the metallic oxide for the development of the full activities. The disulphides were found to be less active than the free thiazoles, both with and without zinc oxide. Replacing the benzene nucleus by an aliphatic residue as in μ -mercaptopthiazoline,



yielded a compound with inferior accelerating power.

Replacement of the sulphur in the thiazole ring, as in 1-mercaptopbenzoxazole,



gave still lower acceleration, and the replacement of the -SH group by -NH₂ or -OH yielded derivatives which were almost inactive.

The vulcanisation of rubber in solution by the interaction of hydrogen sulphide and sulphur dioxide, according to the Peachey method, proceeds more rapidly in presence of benzoquinone.¹¹²

The remarkable activity of the dithiocarbamates and other compounds of the class known as ultra-accelerators is frequently a source of trouble, owing to vulcanisation commencing during the preliminary operations of milling and calendering, and several methods have been devised in order to overcome this defect.

For example, the mixing may be made with all the necessary ingredients except sulphur, which is dusted over the surface when the article is in the shape required. On keeping at ordinary temperatures the sulphur penetrates into the rubber and vulcanisation then proceeds slowly, the degree of vulcanisation being determined by the proportion of accelerator present. This method has been described by E. Romani,¹¹³ although priority is claimed by U. Pestalozza.¹¹⁴

¹¹² Peachey Process Co. and S. J. Peachey, E.P. 190,051; J., 1923, 107A.

¹¹³ Caoutchouc et Gutta Percha, 1922, 19, 11,626; J., 1923, 107A.

¹¹⁴ India Rubber J., 1923, 85, 238; J., 1923, 279A.

Another method described by Romani¹¹⁵ is to incorporate in the mixing the sulphur and other ingredients, and immerse this in a solution of zinc dithiopyromucate in acetone.¹¹⁶ The principle of allowing diffusion of the sulphur and accelerator may also be applied by building up the article from a number of sheets containing alternately, in the one case the sulphur, and in the other case the accelerator,¹¹⁷ and exposing the whole to a suitable temperature; or the sulphur may be introduced into the whole of the layers which contain alternately two compounds which react to give an active accelerator.¹¹⁸

The fact that certain accelerators do not exhibit marked activity may be due to their melting at a temperature higher than that at which vulcanisation is conducted. By mixing two such substances together the melting point is reduced and the activity enhanced.¹¹⁹

One of the characteristics of mixings containing certain accelerators is that the physical properties acquired on vulcanisation remain constant over a somewhat extended period of heating¹²⁰; the importance of this so-called flat-curing or plateau effect lies in the fact that variations in the time of cure do not adversely affect the properties of the vulcanised rubber. This behaviour is particularly evident in the case of the 1-mercapto-3-methylbenzothiazole examined by Scbrell and Boord.¹²¹

Among other compounds which act in a similar manner, the salts of the alkylxanthic acids may be cited¹²²; for example, mixings which contain zinc or cadmium propylxanthate in the presence of zinc oxide may be heated at comparatively low temperatures, from 60° C. to 130° C., when vulcanisation proceeds until a point is reached at which the physical properties remain constant on further heating, even though a considerable proportion of free sulphur is still present.

The effectiveness of accelerators in obscuring variations in raw rubber, which has hitherto been tacitly assumed, has been investigated by G. Martin and W. C. Davey.¹²³ Samples of different kinds of rubber were vulcanised in a mixing containing 10% of sulphur and the times of cure ascertained; these varied from 50 minutes in the case of wet roll from creosoted latex to 115

¹¹⁵ *Loc. cit.*

¹¹⁶ Cf. H. A. Morton, U.S.P. 1,434,908; *J.*, 1923, 64A.

¹¹⁷ M. M. Harrison and H. A. Morton, Assrs. to Millar Rubber Co., U.S.P. 1,434,892; *J.*, 1923, 64A.

¹¹⁸ The Naugatuck Chemical Co. and S. M. Cadwell, E.P. 174,915; *J.*, 1923, 789A.

¹¹⁹ G. H. Stevens and C. H. Eaton, U.S.P. 1,465,743; *J.*, 1923, 1187A.

¹²⁰ C. O. North, *Ind. Eng. Chem.*, 1922, 14, 852.

¹²¹ *Loc. cit.*

¹²² Dunlop Rubber Co., D. F. Twiss, and F. Thomas, E.P. 204,757; *J.*, 1923, 1187A.

¹²³ *J.*, 1923, 98T.

minutes in the case of a sample of crêpe. The same rubbers were then vulcanised at the same temperature in a mixing of rubber 90, sulphur 10, zinc oxide 5, and thiocarbanilide 1; the times of cure necessary to give an elongation of 700% at a load of 0·6 kg. per sq. mm. varied from 10 minutes to 75 minutes. The sample requiring 115 minutes in the pure mixing was vulcanised in 43 minutes in the accelerated mixing, while that curing in 50 minutes required 75 minutes in the presence of accelerator, the order of the rate of cure of the two rubbers thus becoming inverted when employed in an accelerated mixing.

Judging by the attainment of maximum tensile strength, the variation in time of cure was not so pronounced, being reduced from $\pm 26\%$ in the rubber-sulphur mixing to $\pm 17\%$ in the accelerated mixing; similar results were obtained when the coefficients of vulcanisation at a given time of cure were compared. Two rubbers having different rates of cure in a mixing containing sulphur alone, were compounded with zinc oxide and different accelerators, including thiocarbanilide, aldehyde-ammonia, *p*-phenylenediamine, *m*-phenylenediamine, "suparac," and *p*-nitrosodimethylaniline, in the proportions: rubber 90, sulphur 10, zinc oxide 5, accelerator 1. In each case the sample showing the higher rate of cure in a "pure" mixing was vulcanised in a shorter time in presence of an accelerator. A similar investigation carried out by H. P. Stevens¹²⁴ showed that, judging by the extensibility of the vulcanised samples, variations in times of cure were obscured more completely by hexamine than by thiocarbanilide. Latex-sprayed rubber, which was the fastest curing of all the samples examined, preserved this order when accelerated by thiocarbanilide, but in the hexamine mixing the rate of cure was exceeded by a sample of matured slab and by ordinary pale crêpe.

For comparing the activity of accelerators, G. S. Whitby and A. Cambron¹²⁵ introduce the compound into a rubber cement made with xylene and containing sulphur and zinc oxide, the whole being immersed in a bath of boiling water. The contents of the tube are stirred by means of a mechanical stirrer and the time taken for the cement to set to a gel and adhere to the stirrer is noted.¹²⁶ It is stated that the setting point can be ascertained with a fair degree of precision, duplicate experiments giving results within half a minute.

Regarding the theory of the action of accelerators, further evidence in favour of the polysulphide theory of Bedford and his co-workers¹²⁷ has been brought forward by Sebrell and Boord.¹²⁸ The authors find that metallic salts of mercaptobenzothiazoles are

¹²⁴ *Bull. Rubber Growers' Assoc.*, 1923, 5, 292; *J.*, 1923, 667A.

¹²⁵ *J.*, 1923, 333T.

¹²⁶ Cf. Bedford and Sebrell, *Ann. Repts.*, 1921, 6, 368.

¹²⁷ *Ann. Repts.*, 1921, 6, 365.

faster curing than the free compounds and that both types are faster curing than the disulphides. Moreover, the mercapto-benzothiazoles require the presence of metallic oxides in order that they may exhibit their full activity as accelerators. These facts are held to be more in accordance with the theory of Bedford and Sebrell, who regard the zinc salts as giving rise to polysulphides which furnish the sulphur necessary for vulcanisation, rather than that of Bruni and Romani, who regard the disulphides as the intermediate compounds which, by decomposition, yield sulphur in an active form.

W. Scott¹²⁸ regards diphenylguanidine as a hydrosulphide polysulphide accelerator and for its constitution favours the amino structure $C_6H_5\text{NH}\cdot C(\text{NH}_2) : N \cdot C_6H_5$, rather than the imino structure $(C_6H_5\text{NH})_2 : C : \text{NH}$, the hydrosulphide being represented by the formula $(C_6H_5\text{NH})_2 : C : \text{NH}_2\text{SH}$. Although diphenylguanidine decomposes just above its melting point into ammonia, aniline, and triphenyldicarbimide, this decomposition does not occur at normal vulcanising temperatures, and the acceleration is not to be attributed to ammonia produced in this way.

According to E. Romani,¹⁰⁷ it is probable that aldehyde-ammonia and other similar condensation products are first decomposed, yielding ammonia, which gives rise to ammonium polysulphide, and this in turn reacts with the aldehyde to form dithio-acids.

The function of metallic oxides, especially zinc oxide, in promoting the activity of accelerators has been further investigated by C. W. Bedford and H. Gray,¹²⁹ who attribute its action to its maintaining the concentration of the accelerators in the rubber mixing. Hydrogen sulphide is known to precipitate zinc sulphide from zinc dithiocarbamates with formation of free acid, and this reaction will take place in a rubber mixing from the hydrogen sulphide formed by the interaction of the sulphur with the rubber resins. The retarding influence of hydrogen sulphide was demonstrated experimentally by immersing a mixing containing the zinc salt of a dithiocarbamate in the gas for a few hours, after which vulcanisation was shown to proceed comparatively slowly. During normal vulcanisation zinc oxide re-forms the zinc salt and thus preserves the activity of the accelerator. A similar result may be achieved by using excess of the zinc dithiocarbamate, in which case vulcanisation will proceed at ordinary temperatures, even in absence of zinc oxides. Further proof of the mode of action of zinc oxide was afforded by the fact that tetramethylthiouran disulphide could be used in place of zinc oxide in a mixing containing a zinc dithiocarbamate. Small proportions of one of each of these compounds introduced into similar mixings were found no

¹²⁸ *Ind. Eng. Chem.*, 1923, 15, 286; *J.*, 1923, 412A.

to effect acceleration. When, however, the two mixings were combined, the resulting mixture cured very rapidly. This is said to be due to the reaction between the tetramethyldithiouram disulphide and the hydrogen sulphide,¹³⁰ which prevents the latter from decomposing the dithiocarbamate.

Zinc salts of weak acids, such as stearic and oxalic acids, are equally effective. In connexion with the behaviour of zinc oxide, it is pointed out that the function of the zinc oxide may cease during hot vulcanisation owing to the reaction products not being in intimate contact with particles of zinc oxide after a lapse of some little time. In this way the heating may be continued and no apparent vulcanisation take place beyond a certain limit. When, however, the vulcanised sample is removed from the press and allowed to remain at ordinary temperatures, migration of the components of the reaction may take place and the zinc salt of the dithiocarbamate be re-formed and vulcanisation proceed at ordinary temperatures. Figures are quoted showing the effect of storage on a sample which was hot cured until the stage was reached at which no further change in tensile properties occurred on continued heating. On keeping at ordinary temperatures, however, vulcanisation proceeded, and at the end of 75 days a marked change in tensile properties had taken place.

The fact that many accelerators exhibit enhanced activity in presence of bases, such as ammonia and aniline, has been pointed out by several workers,¹³¹ and an explanation of this behaviour is offered by G. S. Whitby and A. Cambron,¹³² whose experiments lead them to conclude that such bases act in a dual capacity. In the first place, the base neutralises the acids which G. S. Whitby and A. R. Winn¹³³ have shown to be present in the acetone-soluble portion of rubber. The solid acid present in *Hevea* resin, a saturated fatty acid, which has been named heveic acid, was shown to retard the vulcanisation of a rubber cement containing an active accelerator; stearic acid behaved in a similar manner.

On the other hand, addition of bases such as ammonia, methyl-aniline, and piperidine, hastened the setting of the cement; addition of small quantities of piperidine, for example, to a cement containing zinc pentamethylenedithiocarbamate effected a marked reduction in the time of setting, but with increasing proportions of the base a point was quickly reached after which further addition did not cause a marked increase in the rate of vulcanisation. This may be explained by assuming that after the resin acids are neutralised the added base ceases to function.

¹³⁰ *Ann. Repts.*, 1922, 7, 326.

¹³¹ G. D. Kratz, A. H. Flower, and C. Coolidge, *Ind. Eng. Chem.*, 1920, 12, 324; Bedford and Gray, *ibid.*, 1923, 15, 723; S. M. Cadwell, E.P. 174,915.

¹³² *Loc. cit.*

¹³³ *J.*, 1923, 336T.

Further experiments showed that not only does the base neutralise the resin acids which, if left in the free condition, would retard vulcanisation, but that the soaps which are thus formed increase the degree of dispersion of the caoutchouc and lead to an increased rate of reaction with sulphur.

In many respects these views supplement those of Le Blanc and Kroger,¹³⁴ who suggested the possibility of comparing the activity of accelerators in solutions and who regard the action of accelerators as affecting the rubber and not so much the sulphur.

An interesting point in connexion with the action of litharge on certain accelerators has been brought to light by P. L. Bean.¹³⁵ In a mixing containing, in addition to rubber and sulphur, piperidine pentamethylenedithiocarbamate and zinc oxide, the additional presence of litharge caused a retardation in the commencement of the vulcanisation, but did not appreciably affect the ultimate time of cure. This suggests a possible method of preventing premature vulcanisation in mixings containing active accelerators.

AGEING.

Some interesting data regarding the mechanism of accelerated ageing of vulcanised rubber have recently been obtained by B. Marzetti.¹³⁶ The effect of heating in different gases at a constant temperature of 77° C was determined, and it was found that whereas samples heated in a sealed tube containing oxygen deteriorated completely, there was no appreciable loss in physical properties when they were heated in an atmosphere of carbon dioxide, or left for a long period in the mould in which they had been vulcanised. The author concludes that ageing is an after-vulcanisation induced by the oxygen of the air, very small proportions of which are sufficient to bring about the destructive change, just as small proportions of sulphur may produce vulcanisation. The ageing of samples vulcanised for different periods of time at 143° C. was examined, and it was found that the velocity of absorption was greater in samples vulcanised for longer times; the rapidity of ageing is therefore held to be a function of the velocity of oxygen absorption, the actual quantity of oxygen required to produce complete physical deterioration being approximately the same for all degrees of vulcanisation. The author also found that with mixings vulcanised to give similar physical properties unaccelerated samples absorbed oxygen much more rapidly than accelerated samples.

Experiments on the natural ageing of rubber vulcanised with the aid of some of the more active accelerators have been described

¹³⁴ *Ann. Repts.*, 1921, 5, 363.

¹³⁵ *India Rubber J.*, 1922, 64, 1051; *J.*, 1923, 106A.

¹³⁶ *Giorn. Chim. Ind. Appl.*, 1923, 5, 122; *J.*, 1923, 464A.

by C. C. Davis.¹³⁷ The accelerators employed comprise diethylamine diethyldithiocarbamate, the dimethylamine and piperidine analogues, and the thiouram disulphides corresponding to these three compounds. Various mixings were used; in one case, smoked sheet 100, sulphur 1, accelerator J, zinc oxide 100, and these were cured for 10 minutes at 30 lb. In nearly every instance, after keeping for two years under ordinary circumstances, the tensile strength was found to be higher than that of the freshly cured sample, and the elongation with a given load had in all cases decreased slightly. The addition of litharge in presence of piperidine pentamethyleneedithiocarbamate as accelerator had no appreciable effect on the rate of cure or the ageing properties.

Very little difference in the tensile or ageing properties was observed even when the proportion of accelerator was halved. With 3 parts of sulphur instead of 1, however, keeping the time of cure of the compounds the same, a marked deterioration had occurred at the end of two years, and this was much more noticeable in the case where 4 parts of sulphur were added. By reducing the temperature of vulcanisation, however, the ageing properties were much improved, and by reducing the time of vulcanisation still better tensile and ageing properties resulted. The author concludes that the use of so-called ultra-accelerators does not lead to more marked deterioration on ageing than is obtained by using the less active accelerators, especially if the vulcanising conditions are chosen with due regard to the proportions of sulphur and accelerator present.

It is generally agreed that rapid ageing is more frequently attributable to an excessive period of vulcanisation than to the harmful influence of compounding ingredients,¹³⁸ but very little work has been done with the object of comparing the ageing properties conferred by various compounding ingredients.

In experiments on the ageing of mixings compounded on the one hand with antimony sulphide and on the other hand with red iron oxide, both largely used pigments, E. Anderson and W. M. Ames¹³⁹ have shown that the ageing properties may be to some extent influenced by the nature of the compounding ingredients used. The pigment was introduced into a simple mixture of rubber (90) and sulphur (10), and also into a mixture in which a proportion of the rubber was replaced by brown vulcanised oil substitute. The samples containing antimony sulphide showed consistently better ageing properties than those containing iron oxide, whether the mixing contained substitute or not.

¹³⁷ *India Rubber J.*, 1923, 66, 303; *J.*, 1923, 989A.

¹³⁸ *Ann. Repts.*, 1922, 7, 323.

¹³⁹ *J.*, 1923, 136T.

Some interesting photomicrographs have been obtained by W. M. Ames¹⁴⁰ in the course of experiments on the ageing of vulcanised rubber. Samples of a rubber-sulphur (90 : 10) mixing under-cured, normally cured, and over-cured were kept at 70° C., and samples withdrawn daily from which sections were cut and photomicrographs obtained. In all cases the free sulphur formations increased in size at first, but afterwards gradually broke up and the amount of visible sulphur diminished. This was shown to be due to loss in sulphur from the surface of the sample with consequent migration of sulphur from the centre portions from which the sections were cut. In the case of a sample of vulcanised rubber which had perished at ordinary atmospheric temperatures, the condition of the free sulphur was the same as in the freshly vulcanised sample. This tends to show that the conditions of artificial ageing are not strictly comparable with those of natural ageing. Reference may be made to the proposal for the addition of anti-oxygens, such as tannin or quinol, for the purpose of improving the ageing qualities of raw and vulcanised rubber.¹⁴¹

TESTING.

An apparatus devised by B. Marzetti for the purpose of determining the plasticity of unvulcanised rubber, presumably after mastication, has been described.¹⁴² The rubber sample is enclosed in a strong cylindrical vessel, the lower portion of which terminates in a cone provided with an orifice of suitable dimensions. The apparatus may be kept at any desired temperature by immersing in a bath of glycerin. The upper portion of the cylinder is connected to a supply of compressed air, the application of which causes the rubber to be extruded from the orifice. The length or weight of the strip of rubber extruded in a given time will depend upon the plasticity at the temperatures employed, and a comparison of different samples is thus possible. A rather interesting application of the apparatus is in connexion with the testing of the activity of accelerators. In mixings which do not tend to vulcanise at the temperature of the bath, which may be from 80° to 100° C., the lengths of rubber extruded in successive intervals will be equal for equal times; but if there is a tendency for vulcanisation to set in, as, for example, in accelerated mixings liable to "scorch," the lengths of the strips issuing in a given time will gradually diminish owing to the firming up of the mixing.

A method for determining the resistance of vulcanised rubber to abrasion has been described by W. W. Evans.¹⁴³ Circular rings

¹⁴⁰ *J. Roy. Microscopical Soc.*, 1923, 265.

¹⁴¹ A. Helbronner and G. Bernstein, *Comptes rend.*, 1923, 177, 204; J., 1923, 844A. Cf. E.P. 142,083.

¹⁴² *Giorn. Chim. Ind. Appl.*, 1923, 5, 342; J., 1923, 1033A.

¹⁴³ Amer. Soc. for Testing Materials, June, 1923; J., 1923, 940A.

are stamped out by means of a die from a sheet of the rubber, and after weighing are attached to a steel spool which is fixed to the lower end of a vertical spindle, capable of being driven at the rate of about 130 r.p.m. The samples are kept apart by means of separator rings and immersed in loose carborundum, contained in a box, a "head" of 5 inches of abrasive being allowed. After rotating for 4 hours, the position of the spool is reversed and the test continued for another period of 4 hours. The degree of resistance to abrasion is ascertained by the relative loss in volume of the samples under test; the loss in weight is actually determined, and from a knowledge of the specific gravity the volume loss is calculated.

It is necessary in each case to include a standard sample of a rubber compound of known abrasive properties, and the loss in volume is calculated as a proportion of the loss undergone by the standard. This method has been employed by H. W. Greider¹⁴⁴ in an investigation dealing with the effect of various compounding ingredients on the abrasive properties of rubber, to which reference has already been made. The tests were run at a speed of 170 r.p.m., under which conditions a rise of temperature of the abrasive and samples to 65.5° C. took place. After each test the mixture of carborundum and rubber dust was passed over a screen to remove abraded rubber and any carborundum reduced to a fine mesh during the process. It was found that unless the grain of the carborundum was kept constant variable results were obtained. The results were expressed in terms of the "co-efficient of abrasion resistance," which is the reciprocal of the percentage loss in volume resulting from the test after a standard number of revolutions, in this case 100,000, or approximately 10 hours' rotation in the abrasive.

An abrasion testing machine of the fixed type is described by H. A. Depew,¹⁴⁵ and consists essentially of a circular turntable provided with an abrasive track made by casting a mixture of Portland cement and abrasive quartz. The samples of vulcanised rubber to be tested are held in position against the surface of the track, which rotates at the rate of about 30 r.p.m. The track is kept free from abraded rubber by means of stationary brushes, and suction pipes are placed at intervals to carry away the dust. In a comparison of results obtained by this method and the loose abrasive method described above, the author found¹⁴⁶ that the values obtained were of the same order over a range of samples, but that the loose abrasive method tended to emphasise the difference between a good and a poor resisting sample.

¹⁴⁴ *Ind. Eng. Chem.*, 1923, 15, 504; *J.*, 1923, 615A.

¹⁴⁵ *India Rubber World*, 1923, 68, 357.

¹⁴⁶ *Ibid.*, 1923, 68, 566.

The measurement of temperature in rubber, particularly in tyres, by means of thermocouples has been studied by E. B. Spear and J. F. Purdy,¹⁴⁷ who find that the temperatures recorded are liable to be much too low unless the wires are embedded in the rubber for some distance from the thermal junction. The authors have devised a new type of thermocouple specially adapted for taking the temperature of tyres during running tests.

The mechanical testing of rubber has been discussed by G. S. Whitby,¹⁴⁸ who compares the ring-shaped test piece with the straight or dumb-bell type. The method of plotting tensile curves in which the strains are recorded as abscissæ and the stresses as ordinates is favoured.¹⁴⁹

ANALYSIS.

The methods at present in use for the analysis of rubber are probably of a very diverse character, each laboratory favouring its own special procedure. In cases where the analysis is carried out in order to ascertain whether the material is in agreement with the requirements of specifications, the adoption of standard methods of analysis would be to the advantage of both the consumer and the manufacturer. For the past year or two a committee of the Rubber Division of the American Chemical Society, acting in conjunction with a sub-committee of the American Society for Testing Materials, has been engaged on the task of formulating methods of analysis which will be acceptable to all concerned. The tentative scheme originally recommended has been discussed and slight modifications and additions introduced; the complete scheme, as finally approved, has now been published and will be seen to embrace, in addition to the older analytical processes, determinations of free carbon, glue, and cellulose.¹⁵⁰

The aid which the microscope may render in the examination of vulcanised rubber articles is indicated in a communication by W. M. Ames,¹⁵¹ who shows photomicrographs of sections of rubber containing glue and rubber substitute.

¹⁴⁷ *Ind. Eng. Chem.*, 1923, **15**, 842; *J.*, 1923, 1033A.

¹⁴⁸ *India Rubber World*, 1923, **67**, 362.

¹⁴⁹ Cf. W. B. Wiegand, *Ann. Repts.*, 1922, **7**, 328.

¹⁵⁰ *Ind. Eng. Chem.*, 1923, **15**, 308.

¹⁵¹ *J. Roy. Microscopical Soc.*, 1923, 265.

LEATHER AND GLUE.

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THERE has been a gradual but general improvement in trade during the past twelve months, in which most sections of the leather industry have participated. It is difficult to trace the source of this improvement. The boot and shoe manufacturers disclaim any improvement in trade, but export returns and employment returns are against them. Many factories in the Northampton district are working full time and some even on overtime, notwithstanding that this is the slack time in the boot and shoe trade.

The boot and shoe industry, as well as the leather trade, has enlarged its productive capacity by several times during the last ten years. Some leather works have a capacity for turning out five times as much leather as they did in pre-war days, and until the slump came in 1921 they were manufacturing at full pressure; even now they are dressing much more than their pre-war output. Hides have touched the lowest figure and there has been a slight increase in price. There is not a great deal of unemployment in the leather and allied trades. Repeated attempts have been made to force up the prices of hides, but without success.¹ In the case of sheepskins, however, prices are being increased, the United States being responsible for a great deal of the high-priced raw material. In July nearly two million woolskins were sold to the States, as compared with 34,000 in the same month of the previous year. For the seven months ended July we shipped nearly 3½ million skins, as against 400,000 for the same period of 1922. For the eight months ending August, 1923, the exports of English woolled skins were 13,844 cwt., against only 4843 cwt. for 1922.

During the last three months of 1923, the wages of American shoe operatives have been increased by 11%, which brings them back to the war-time peak.² The suggestion was put forward in last year's Report that there must be a scarcity of leather in the States, otherwise British tanners would not be finding such a profitable outlet for their productions in that country. American suede calf has been difficult to obtain for some time past. Practically no American sole leather is being imported into this country, and with the exception of glazed kid and patent leather, very little high-grade leather is coming from America.

¹ Cf. *Ann. Repts.*, 1922, 7, 334.

² *Leather Trades Rev.*, 1923, 842.

Sole leather tanners are enjoying a period of prosperity which is unique in many respects. There is an absence of American competition and exchange vagaries render French competition speculative and unreliable. The raw materials have slumped to very low limits. Tanning materials have been remarkably cheap, but a reaction has set in. The shortage in home supplies of raw hides has been counterbalanced by foreign supplies of dried and dry-salted hides. On the other hand, shoe manufacturers have been exceedingly keen to purchase low-priced leather, and it has been impossible to obtain any advance in prices, which are almost pre-war.

The demand for cheap sole leather is being met by changed methods of manufacture. Before the war sole leather was given "suspenders," "handlers," "layers," and "dusters," and the tannage required about three months or longer. Some of the larger tanyards had proved the efficacy of motion during tannage, and hides were enclosed in lattice drums in the liquors and the drums could be revolved during the process. This principle was extended very considerably during the war, and sole leather is now being tanned in from three to five weeks.

The finished product is firm, waterproof, and cheap. It contains a high percentage of water-soluble matter, but according to a recent research³ this is not detrimental to the wearing properties. The supremacy of the British heavy leather industry is very gratifying in view of the fact that most of the leather trades chemists are employed by that branch of the trade. The achievements of the British tanner are due in no small degree to the extract manufacturers, and some of the most eminent chemists connected with the leather trade are devoting their energies to this branch of the industry.

The chrome leather industry is reviving. Mention was made in last year's report⁴ of its terrible plight owing to foreign competition. Several firms have been able to meet this competition, whilst others have marked time until recently. The French occupation of the Ruhr has impeded trade with that district, and at the time of writing encouraging reports are being received from all the manufacturers of chrome calf, as they are finding a greater demand for their productions. Suede and white calf find a very ready market, but producers are hesitating before extending their productive capacity on such luxury leathers. Glazed kid is being manufactured in greater quantity, but much prejudice is arising owing to the unscientific methods of production practised by several individual firms. There is an urgent need for the application of more science to this branch of the leather trade, which is essentially chemical tanning, but the difficulty appears to be in

³ U.S. Dept. of Agric. Bull. No. 1168; J., 1923, 1142A.

⁴ Ann. Repts., 1922, 7, 338.

securing the right type of trained individual. Either the chemist is not practical or the practical man has not had the opportunity of a training. It is very difficult to combine efficient training in both theory and practice.

There is the same difficulty in connexion with leather dyeing. Several of the most important leather manufacturers appear to have realised the need for a man who has a practical knowledge of dyeing and yet who is a highly trained chemist with a thorough knowledge of the chemistry of dyestuffs. Such men are very difficult to obtain, and possibly there are not more than half-a-dozen in the country. Yet the writer believes that there is a great field for those who can apply their knowledge to the particular problems of leather dyeing and finishing. Such men always improve the standard of production, and that is an achievement in these days of keen competition. There are many problems, such as fading, the effect of fat liquoring, and difficulties in finishing, which are essentially applied chemistry.

There have been two notable contributions to the literature of the trade. M. C. Lamb's "The Manufacture of Chrome Leathers"⁵ is a most excellent book, and will prove a valuable aid to this branch of the industry. It is the first English publication on this subject and is, therefore, the more welcome. It describes the preparation of the pelt for tanning, the one-bath and two-bath methods of chrome tanning, and the finishing of different kinds of leathers. J. A. Wilson has published a book on "The Chemistry of Leather Manufacture,"⁶ which is unfortunately spoilt by the author's strong personal views on the theory of tanning, bating, and methods of tannin analysis.

The Society of Leather Trades Chemists held its biennial conference at Barcelona in September, and some important alterations were made in the methods of analysis, which are described later. Official methods have been adopted for the analysis of chrome-tanned leathers. Dr. Pickard, Director of the British Leather Manufacturers Research Association, delivered two lectures⁷ on November 29th, and described the results of the recent work of that association. Some reference to that work is also given below.

R. Kissling⁸ has published a book on "Glue and Gelatin" in German. It is a practical work and contains very little chemistry. It describes the manufacture of gelatin and glue in detail, and contains a very large list of references to patents. One section is devoted to the valuation of glue, gelatin, by-products, and raw materials. J. Alexander⁹ has written a monograph on the same

⁵ *Chem. and Ind.*, 1923, 738.

⁶ *J. Soc. Leather Trades Chem.*, 1923, 7, 457.

⁷ *Chem. and Ind.*, 1923, 1213.

⁸ *Ibid.*, 1923, 838.

⁹ *Ibid.* 1923, 847.

subject, which furnishes a well-digested survey of the research work already done on these materials. The chemistry of glue and gelatin is treated very ably, and considerable stress is laid on the importance of hydrogen-ion concentration. The author expresses the view that no one has hitherto made or experimented with chemically pure gelatin. The ash and water content of the gelatins used in various researches is rarely stated. The best book on this subject is one published at the close of 1922 by R. H. Bogue¹⁰ on "The Chemistry and Technology of Gelatin and Glue," a comprehensive work of 644 pages. It is of the greatest value to the chemist in the glue and gelatin trade, as a large portion of the book is devoted to the testing of glue and gelatin. A large number of physical and chemical methods is described, and the author emphasises the importance of determining the p_{H} value of a 1% solution of glue. He also includes an account of most of his own work dealing with the uses of glue as an adhesive, and he deals fully with the factors affecting the strength of a glued joint.

CURING AND SOAKING.

Curing and soaking have been scientifically investigated during the past two or three years, and the investigations have resulted in some interesting discoveries.

G. D. McLaughlin and G. E. Rockwell¹¹ have continued their researches on the bacteriology of the curing of hides and skins. There are various factors which influence the growth of bacteria on hides and skins during the curing process. A certain amount of salt is necessary to inhibit the growth of bacteria. From 10 to 16% of salt is necessary in the absence of blood, dirt, etc. The presence of nutritive materials in the brine, such as blood, manure, dissolved hide substance, etc., favours the growth and development of bacteria and necessitates the use of larger percentages of salt in order to produce any inhibitory effect. The present methods of curing are most unfavourable for their purpose. The proportion of skin to brine is greatest, there is a high concentration of blood in the brine formed in the skins, the repeated use of salt increases the amount of protein matter which it contains, and there is a grave danger of the brine becoming alkaline due to the putrefaction of the blood and protein. The skins should be thoroughly washed and brined, then salted. In this way the blood and dirt will be removed before brining, the proportion of weight of skin to brine can be regulated, the reaction of the brine can be controlled, and the rate of diffusion of salt into the skin is a maximum.

R. H. Pickard¹² states that the difficulty of softening back-dried

¹⁰ *J.*, 1922, 576n.

¹¹ *J. Amer. Leather Chem. Assoc.*, 1923, 18, 233; *J.*, 1923, 732A.

¹² *Leather Trades Rev.*, 1923, 944; *Chem. and Ind.*, 1923, 1213.

hides is due to the coagulation of the "hide albumins," particularly the cementing substance, and sodium citrate solution softens such hides very quickly. One piece was softened by this means in $\frac{1}{4}$ hour. Before the dried hide or skin can be rendered responsive to water, lime, or tan, this coagulated cementing substance must be removed in order to separate the fibre and fibrils. The use of trypsin for its removal has been provisionally protected.

G. D. McLaughlin and E. M. Theis¹³ have continued their work on curing processes. They showed in their previous work that the time between flaving and salting had a great influence on the yield of leather and the amount of swelling given by the hide. In their most recent work they have compared the properties of "Frigorifico" hides and "native" hides. Frigorifico hides are first washed with water, and then immersed in a saturated salt solution for a number of hours prior to salting. Native hides are salted without washing or brining. Native hides decomposed much more rapidly than Frigorificos, as shown by the amount of ammonia formed on leaving pieces of each in water in a closed vessel for several days. At the end of the eighth day the native hide had lost 10% of its weight. A 10% salt soak instead of water checked this loss and reduced it by half in a period of 8-11 days. Hide soaked in plain water lost 8.33% of its weight during the soaking period, whereas hide soaked in 10% salt solution gained 8.33% over its original weight. It has been shown that the difference between a salt soak and water is not due to the absorption of salt by the hide, because the whole of the salt will diffuse out again in 48 hours. Increased temperature stimulates the production of ammonia and the hydrolysis of the salted hide. Dissolved protein matter, blood, or similar material increases the amount of hydrolysis. Further experiments have shown that the ash content of the hide diminishes during soaking. The mineral salts present in the skin consist of sodium, potassium, calcium, magnesium, silica, aluminium, and iron compounds. When fresh corium is soaked in water the physiological mineral constituents diffuse out, water diffuses in, and some of the protein is dissolved. The ash of the corium diminishes from 0.37% to 0.14% in two hours, and 0.065% in six hours. When fresh corium is soaked in water containing the physiological salts in the same proportions as they are present in the corium there is a much less rapid loss of ash, but a slight increase in the amount of protein dissolved. The most significant feature of the loss of mineral matter by the corium is its effect on its swelling power. The following table shows this:—

| | | Water. | Physiological salt solution. |
|------------------------------|----|--------|---------------------------------|
| Swelling in 24 hours .. | .. | 4% | 16% |
| Original ash lost in soak .. | .. | 86% | 19% |

¹³ J. Amer. Leather Chem. Assoc., 1923, 18, 207; J., 1923, 899A.

The paper concludes with the following remarks :—“ We note that skin hydrolysis is affected by previous history and method of curing, and the manner in which it is soaked. If, in curing skin, we soak it in water unduly, prior to brining or salting, an irreversible change in the skin ensues. If, in soaking the cured skin in the tannery, certain conditions noted exist, a rapid decomposition of the skin is brought about.” In a further paper,¹⁴ the same authors deal comprehensively with the science of soaking ; their findings up to date may be summarised as follows :—(1) Previous history and curing of skin, (2) water content of skin when soaked, (3) direction of movement of substances into and out of skin, (4) character of protein dissolved, (5) character of soak water, (6) concentration of salt in soak and rate of its outward diffusion, (7) acidity or alkalinity of soak, (8) temperature, (9)* proportion of weight of skin to weight of soak water, (10) period of soaking, (11) effect of changing soak water, (12) chemical effect of antiseptics, (13) composition of soak waters from various tanneries. The previous history of a hide has a great influence on the soaking. Partially decomposed hides required a modified soak. “ Native ” hides are not as well cured as “ frigorificos.” The cure in frigorificos is more uniform, and hence the swelling of the hides in the soak is also more uniform. The drier a hide the longer is the period of soaking required. In curing with salt, the bulk of the salt enters through the flesh side of the hide, and in soaking it leaves on that side. If hides are fleshed before soaking they lose more protein matter than unfleshed hides. The inorganic and organic constituents of soak waters affect the swelling and soaking of hides. Ferrous sulphate and magnesium sulphate in a water produce great swelling, probably owing to the hydrolysed acid. Salt solutions produce less swelling than distilled water. As the concentration of the sodium chloride solution is increased, the amount of nitrogen present as ammonia in the soak is diminished, and the amount of uncoagulable nitrogen also diminishes, showing that less collagen is dissolved in a stronger salt solution. Acids and alkalis increase the amount of swelling produced, and also the amount of hydrolysis. As the temperature of the soak water rises, the development of bacteria increases, and more of the skin is dissolved, with the consequent decrease in soak and “ white weight ” gains. As the proportion of soak water increases, a greater percentage of protein is dissolved, a greater degree of hydrolysis occurs, and the rate of outward diffusion of sodium chloride is increased. If too small a proportion of soak water is used the swelling in soaks and limes is lessened, and the softening of the skin is slower. There is an optimum period of time for soaking at each given temperature with a given skin. Beyond this, positive

¹⁴ J. Amer. Leather Chem. Assoc., 1923, 18, 324 ; J., 1923, 899A.

damage may result. • The more frequently a soak water is changed for one and the same hide, the greater is the total amount of nitrogenous matter dissolved, and the lower the "white weight" gain. Antiseptics do not appear to diminish either the swelling power or the amount of hydrolysis. A new antiseptic¹⁵ has been discovered for anthrax. Hides are soaked in weak solutions of iodine in water or in carbon tetrachloride. A 0·5% solution is effective if the proportion of skin to solution is not more than 1 : 9, or the hides can be disinfected with iodine vapour. The iodine vapour or solution discolors the hides, but the discolouration can be removed by means of solutions of sodium thiosulphate.

LIMING, BATING, ETC.

B. Hennig and A. Lottermoser¹⁶ have studied the adsorption curves of alkalis and sulphides by hide powder. The use of alkali bisulphides for unhauling hides and skins has been patented.¹⁷ F. Clotofski¹⁸ has shown that hides and skins lose 10–15% of hide substance during liming unless the lime liquor already contains hide substance. A baryta liquor saturated with hide substance dissolves practically no hide substance, although a baryta solution has a greater solvent action on hide substance than a lime solution. E. Stiasny and R. Wurtenberger¹⁹ find that an equilibrium exists between the calcium sulphide and calcium thioarsenite in an arsenical lime liquor. On the gradual addition of lime water to red arsenic, calcium thioarsenite is formed and it reacts with more lime to form calcium sulphide and arsenite. The whole of the sulphur in arsenic disulphide and trisulphide is converted into calcium sulphide by repeated treatment with lime water, whereas only a portion of the sulphur in arsenic pentasulphide is thus converted into calcium sulphide. These authors have shown that milk of lime and red arsenic react completely with each other in the cold if the components are finely divided and well shaken together, whereas the view has always been held that red arsenic and lime only reacted when warm. Polysulphides are always formed in limes made from arsenic pentasulphide. Atmospheric oxygen diminishes the hydrosulphide-ion concentration, causes the formation of quinquevalent arsenic compounds, and increases the amount of sulphur rendered ineffective by the formation of thioarsenate. Red arsenic should be free from arsenic pentasulphide and arsenic trioxide. The maximum amount of calcium sulphide is obtained by avoiding oxidation and by having the red

¹⁵ *J. Amer. Leather Chem. Assoc.*, 1923, 18, 541; *J.*, 1923, 1188A.

¹⁶ *Kolloid-Zeits.*, 1923, 32, 51; *J.*, 1923, 236A.

¹⁷ E.P. 191,431; *J.*, 1923, 237A.

¹⁸ *Collegium*, 1922, 847; *J.*, 1923, 319A.

¹⁹ *Ibid.*, 1923, 43; *J.*, 1923, 616A.

arsenic and lime as finely divided as possible. U. J. Thuau and M. Massin²⁰ have patented a process for unhairing skins by submitting them to the action of liquid air. J. A. Wilson and A. F. Gallun, jun.,²¹ have unhaired skins by means of pancreatin.

J. L. Collett²² of the British Leather Manufacturers Research Association has published an account of some work carried out on the presence and survival of bacteria in lime liquors. He concludes that bacteria may survive in lime liquors but they cannot develop, and therefore liming effects cannot be attributed to them. F. C. Thompson²³ records the existence of other views, and states that some still feel that bacteria can play a part in liming. W. Moeller²⁴ finds that liming hydrolyses proteins to peptones in the first stage. Old limes contain bacteria, and these yield ferment which hydrolyse the peptones to amino-acids, and in this way the action of the lime approaches that of a bate. In the bating process the simpler proteins are hydrolysed to polypeptides, peptides, and amino-acids, which take no part in the tanning process. Elastin fibres, muscles, nerves, blood vessels, and other structures containing aromatic complexes, e.g., tyrosine, are attacked in the later stages of liming and in bating. White collagen fibres are practically unaffected by bating. Owing to the specific action of enzymes, artificial Bates can never replace the natural Bates. Artificial Bates to be as effective as natural Bates must be prepared from the enzymes from living organisms.

C. S. Hollander²⁵ has published some interesting studies on the strength of proteolytic enzymes during the process of bating. He has shown that old limes rich in bacteria have a considerable effect in breaking down the elastin fibres, and probably have a similar action on the rest of the skin. This effect seems to be continued in each of the subsequent processes. The comparatively short washing after liming produces a very striking effect on the elastin fibres. The modification of the elastin fibres is not a function of the bating operation alone, but of all the beam-house processes in varying degree. In this regard it is fitting to note a paper by A. W. Thomas and F. L. Seymour-Jones²⁶ on the hydrolysis of collagen by trypsin. The acidity of the pre-treatment and digestion was controlled, and the effects of varying the time of digestion, concentration of the enzyme, and the size of the collagen particles were examined. Hide powder was used as the form of collagen. The optimum hydron concentration for the

²⁰ E.P. 200,763; *J.*, 1923, 900A.

²¹ *Ind. Eng. Chem.*, 1923, **15**, 267; *J.*, 1923, 367A.

²² *J. Soc. Leather Trades Chem.*, 1923, **7**, 415; *Abs.*, 1924, B, 25.

²³ *Ibid.*, 1923, **7**, 394; *J.*, 1923, 1084A.

²⁴ *Z. Leder- u. Gerb.-Chem.*, 1921, **1**, 232; *J.*, 1923, 107A.

²⁵ *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 638; *J.*, 1923, 108A.

²⁶ *J. Amer. Chem. Soc.* 1923, **45**, 1515; *J.*, 1923, 734A.

hydrolysis was found to be at $p_{\text{H}} 5.5$. Previous treatment of the collagen with solutions of various degrees of acidity did not influence the subsequent trypic digestion. The speed of hydrolysis increased as the size of the collagen particles diminished. It is thought that the action took place at the surface of the particles. Hydrolysis increased with increasing concentration of the trypsin, but it never reached completion under the limits of the experimental conditions employed. The maximum amount of hydrolysis obtained was 76%. These results negative most of the previous ideas held in regard to collagen, viz., that trypsin acts on all soluble proteins, but not on all insoluble ones, e.g., collagen. These results are confirmed by the studies of E. Stiasny and W. Ackermann,²⁷ who find that the action of trypsin on collagen in the presence of neutral salts depends on the degree of swelling of the collagen. Potassium thiocyanate, iodide, nitrate, and chloride give moderate swelling with $N/100$ and $N/10$ solutions, a sharp maximum with $N/1$ solutions, and repression with more concentrated solutions. Potassium sulphate gives a maximum with $N/10$ solutions. The swelling is greater at 37° C. than at 20°. If the anions are arranged in order of the maximum swelling they produce they agree with the Hofmeister series. This is also given by solutions of the same p_{H} value, thus contradicting the views of Loeb, who contests the Hofmeister series. Numerous experiments have shown that potassium thiocyanate solutions of $N/100$ and $N/10$ strength have no appreciable influence on the action of the trypsin, but $N/1$ solutions increase the proteolytic action of the trypsin very much. The hide powder is dissolved completely. The peptolytic action of the trypsin is diminished, and both effects are inhibited by $5N$ solutions. The influence of the potassium thiocyanate corresponds with the degree of swelling. Increased concentration of trypsin and temperature have slight effects on the action of the trypsin, but they do not affect the connexion between the swelling and the proteolytic effect. The same relationship holds with potassium iodide, chlorate, and sulphate in their effect on the action of the trypsin. In the case of potassium nitrate and chloride the effect of the salt on the enzyme appears to be greater than its effect on the hide substance, and no maximum protolytic effect is obtained with $N/1$ solutions. The peptolytic effect of trypsin is not parallel with the proteolytic effect. Hide powder is more susceptible to the action of trypsin than pelt.

The Röhm and Haas Co.²⁸ has carried out experiments on goatskins which show that an old lime has a considerable effect in breaking down elastin fibres. This effect is continued in each of the subsequent processes. The short washing after liming has an

²⁷ *Collegium*, 1923, 74; *J.*, 1923, 733A.

²⁸ *J. Amer. Leather Chem. Assoc.*, 1923, 18, 516; *J.*, 1923, 1188A.

appreciable effect on the elastin fibres. The modification of the elastin is not a function of the bating operation only, but of all the beam-house processes in varying degrees. The change in the elastin fibres is possibly not the only change which takes place in the wet work, but the effects on the other constituents of the skin cannot be studied so easily. W. Moeller²⁹ has patented a process for liming and bating hides with the freshly dried constituents of the pancreatic gland and dog's dung, which are extracted with 0·1% solution of calcium hydroxide or magnesium hydroxide or both.

TANNING AND TANNING MATERIALS.

A number of new tanning materials have been reported on during the year. Heim and Cercelet³⁰ have analysed numerous barks from trees in the Madagascar forests and note several which could be utilised by tanners in this country. Rotra bark (*R. fotsy* and *R. meno*) is a thick, fibrous bark containing 12·62% of a mixed tannin and 12·17% of soluble non-tans. Lalona (*Weinmannia bojeriana*) bark is a thin bark which is not so easily extracted; it contains 13·75% of a mixed tannin, 2·68% of soluble non-tans, and yields a fairly soft leather which is not so dark-coloured. Filao bark (*Casuarina equisetifolia*) contains 15·31% of an easily extracted catechol-tannin, 3·65% of soluble non-tans, and yields a light-coloured leather. Badamier bark (*Terminalia Catappa*), also known as Hatafa, is a thin bark, which contains 11·81% of an easily extracted pyrogallol-tannin, 4·44% of soluble non-tans, and yields a soft, light-coloured leather.

A large portion of French Cochin China is covered by forests which contain some useful trees for the tanner. Heim and Cercelet³¹ have analysed a number of oak barks from that country, and they appear to be of promise to the tanner. The first is *Quercus pseudo-cornea*, which contains soluble tans 12·2-18·2%, soluble non-tans 4·1-7·1%. *Castanopsis sinensis* shows soluble tans 13·3%, soluble non-tans 3·9%, which is an excellent proportion of tans to non-tans. Most of the barks are easily extracted, giving a liquor which keeps fairly well. The liquor gives a soft, dry tannage with a very pale colour. There are a large number of varieties of *Quercus pseudo-cornea*, a few of which are very poor in tannin content, but many of the varieties examined contain a workable percentage of tannin and only a small amount of non-tans so that they should prove of real value to the tanner and extract manufacturer in search of new supplies of raw materials. At present China and Japan absorb the available supplies of cut

²⁹ E.P. 199,937; *J.*, 1923, 900A.

³⁰ *J. Soc. Leather Trades Chem.*, 1923, 7, 361; *J.*, 1923, 1088A.

³¹ *Le Cuir*, 1923, 86; *Leather Trades Rev.*, 1923, 191.

bark, but there is a large reserve which could be tapped if the demand was forthcoming.

Heim and Schell³² have reported on a number of samples of mangrove barks from Madagascar. They emphasise the fact that the use of mangrove as an adulterant has brought this material into serious disrepute. They describe the different barks found along with mangrove, all of which contain some tannin. The Freiberg Research Station³³ has already done some work on mangrove barks from South-West Africa, and the results showed that only the barks of *Rhizophora*, *Bruguiera*, *Ceriops*, and *Xylocarpus* were of importance. The tannin contents of these were as follows :—*Rhizophora*, 28–42% tans ; *Bruguiera*, 28–42% tans ; *Xylocarpus*, 27–33% tans ; *Ceriops*, 24–32% tans. Large quantities of mangrove are used in Germany for making mixed extracts. Samples of different barks from Madagascar have been analysed and tested on pelt by the French Colonial. The products analysed were Honkolahy, Tsitodona, and Honkovavy mangrove barks, and others which were not so plentiful. The following results were obtained :—

| | Tans. | Non-tans. | Moisture. |
|-----------------|-------|-----------|-----------|
| | % | % | % |
| Honkolahy | 34.96 | 11.04 | 14.6 |
| Tsitodona | 27.23 | 6.91 | 16.2 |
| Foby | 23.78 | 7.28 | 13.7 |
| Honkovavy | 23.42 | 7.48 | 12.4 |

Honkolahy, Tsitodona, and Honkovavy give a satisfactory tanning, with good penetration and a fairly full tanning which dries out fairly soft. Foby (*Carapa obovata*) gives poor results in tanning tests, the pelt is not completely penetrated, and it dries out hard, although it has a high tannin content. This shows the need for selecting the species of so-called mangrove barks which are used if the best results are to be obtained in leather manufacture.

Various patents³⁴ have been taken out for improvements in tanning and in the extraction of tanning materials. The principle of speeding up by motion is applied to leaching ; R. Rieder³⁵ revolves or agitates the finely divided tanning material in the leach liquor. Various new tanning condensation products have been discovered.³⁶

A. N. Srivastava³⁷ has published the results of an investigation of the loss in tannin content of myrobalans during the drying process. The fruit is gathered in the forests of India, and spread out to dry, which occupies from fifteen to twenty days. In the

³² *Le Cuir*, 88 ; *Leather Trades Rev.*, 1923, 192.

³³ *Lederotechn. Rundsch.*, 1911.

³⁴ E.P. 200,203 ; J., 1923, 845A. E.P. 200,979 ; J., 1923, 991A.

³⁵ G.P. 367,496 ; J., 1923, 512A.

³⁶ E.P. 200,262 ; J., 1923, 845A. U.S.P. 1,460,422 ; J., 1923, 846A.

³⁷ J., 1923, 272T.

first series of experiments, a sample of almost ripe fruit was divided into two parts, each of which was dried in the shade three days, but one portion was crushed. The crushed sample then contained 27.5% of tannin, and the whole sample 20.0%. The crushing had resulted in a conservation of some of the tannin, and the colour of the crushed sample was brighter. The conclusion arrived at was that the drying process requires to be accelerated. Further tests were made with crushing and slicing:—Crushed, 27.5% tannin; sliced, 28–28.5%, tannin. Some varieties of myrobalans are very liable to attack by moulds in presence of moisture. The tannin content is sometimes halved as a result of such attack, and the colour becomes more yellowish. The infection can be avoided by the use of 0.5% of toluene or 0.25% of phenol, or by treatment with sulphur dioxide.

THEORY OF TANNING, ETC.

Additional evidence of the chemical individuality of Chinese tannin has been discovered by J. Herzig.³⁸ M. Nierenstein³⁹ criticises much of K. Freudenberg's work.⁴⁰ He has shown⁴¹ that "Paullinia tannin" is a normal glucoside and not an acyl derivative of glucose. M. Nierenstein⁴² has also examined a gallo-tannin which yielded such a small amount of dextrose that its optical properties must be due to an optically active leuco-digallic acid and not to the sugar. He⁴³ has also continued some researches on the pentamethyl derivative of catechin C, which is present in root gambier and Pegu catechu. P. Karrer, H. R. Salomon, and J. Peyer⁴⁴ have produced evidence which establishes the fact that the tannin fractions of higher rotatory power from Chinese tannin must be derived from pentagalloylglucose. K. Freudenberg⁴⁵ has separated the *l*- and *dl*-catechins and *l*- and *dl*-epicatechins from the ethereal extract of *Acacia Catechu*.

O. Gerngross and H. Loewe⁴⁶ find that pelt treated with formaldehyde absorbs much more alkali than untreated pelt, and they infer that there is a chemical action between the basic groups in the hide protein and the formaldehyde. W. Moeller's theory⁴⁷ of the mechanical enclosure of the hide fibrils by the formaldehyde does not explain the increased power of the hide to adsorb alkali.

³⁸ *Ber.*, 1923, **56**, 221; *J.*, 1923, 192A.

³⁹ *Ber.*, 1922, **55**, 3831; *J.*, 1923, 108A.

⁴⁰ *J.*, 1922, 607A.

⁴¹ *Chem. and Ind.*, 1923, 501.

⁴² *Analyst*, 1923, **48**, 321; *J.*, 1923, 990A.

⁴³ *Ber.*, 1923, **56**, 1877; *J.*, 1923, 1083A.

⁴⁴ *Helv. Chim. Acta*, 1923, **6**, 3; *J.*, 1923, 280A.

⁴⁵ *Ber.*, 1923, **56**, 1185; *J.*, 1923, 616A.

⁴⁶ *Collegium*, 1922, 229; *J.*, 1923, 23A.

⁴⁷ *Ann. Repts.*, 1922, **7**, 355.

W. Moeller⁴⁸ has replied to this. A. W. Thomas and S. B. Foster⁴⁹ find that in all tannin solutions, except quebracho, the tannin particles are positively charged below p_{H} 2·0 and negatively charged at and above p_{H} 2·5.

J. S. Rogers⁵⁰ has compared the plumping action of various concentrations of acetic and lactic acids, and finds that the same titratable acidity does not produce the same plumping. The presence of tannin lowers the plumping effect produced by these acids. He has used the Caffin method with success. E. C. Porter⁵¹ has continued his work on the swelling of hide powder, using solutions of neutral salts. Neutral salts have a greater repressive action on acid-swollen powder than on alkali-swollen powder. The presence of sodium chloride increases the amount of hydrolysis of the hide substance. Porter suggests that the sodium chloride actually increases the activity of the hydrogen or hydroxyl ion. J. A. Wilson and A. F. Gallun, junr.,⁵² have obtained two points of minimum plumping of calf skin, one at p_{H} 5·1 and the other at p_{H} 7·6, but W. R. Atkin⁵³ attributed one of these to the presence of salts and affirmed that there was only one point of minimum plumping, viz., p_{H} 4·7. W. Moeller⁵⁴ has recapitulated the physical theory of tanning. Lining with alkalies or swelling with acids causes a partial breaking up of the micells and a small amount of hide substance is lost. All tanning agents prevent hydrolysis. Synthetic tannins are really strong acids and act as such. Free hydrogen ions have a destructive effect on hide substance, and all ionic theories of tanning are therefore in his opinion wrong. The essential constituent of a tanning solution is an absolutely insoluble substance or a substance which forms an insoluble product in contact with the hide substance. This substance must be converted into a colloid sol by peptisation. Leather is produced by the adsorption and deposition of the insoluble peptised substances on the individual micells of the micellar bands. Although many chemists do not believe in Moeller's peptisation theory, recent scientific work is confirming the most essential part of it. J. Alexander⁵⁵ has pointed out that there are three colloidal elements in pelt. Coarse particles of tanning agents lack diffusibility. Protectors tend to deflocculate the tannin; low p_{H} tends to coagulate it. R. J. Browne⁵⁶ has prepared collodion filters

⁴⁸ Z. Leder- u. Gerb.-Chem., 1922, 2, 252.

⁴⁹ Ind. Eng. Chem., 1923, 15, 707; J., 1923, 844A.

⁵⁰ J. Amer. Leather Chem. Assoc., 1922, 17, 611.

⁵¹ J. Soc. Leather Trades Chem., 1922, 6, 417; J., 1923, 152A.

⁵² Ind. Eng. Chem., 1923, 15, 71; J., 1923, 236A.

⁵³ J. Soc. Leather Trades Chem., 1924, 8.

⁵⁴ Z. Leder- u. Gerb.-Chem., 1922, 2, 45; J., 1923, 511A.

⁵⁵ J. Amer. Leather Chem. Assoc., 1923, 18, 400; I. T. R., 1923, 856.

⁵⁶ Ibid., 1923, 18, 409; J., 1923, 989A.

which could remove the whole of the soluble matter from a tannin solution, others which removed a portion of the tannin, whilst some were capable of filtering off the tannin only; these results indicate that the differentiation of tannins from non-tannins is merely one of size of colloidal particles.

D. Burton, R. P. Wood, and A. Glover⁵⁷ have continued their valuable researches on chrome tanning. They have compared the precipitation figures of a series of violet and green chrome liquors with the hydron concentrations. The precipitation figure is a function of the initial hydron concentration, and it has been found possible to calculate the initial hydron concentration from the precipitation figure. The precipitation figure is dependent on the nature of the basic chromium, the temperature, and the constituents of the solution. They have also studied⁵⁸ the tanning properties of several chrome liquors. The rate of adsorption from liquors reduced with glucose, sulphur dioxide, and sawdust respectively and neutralised chrome alum solution, increased in the order given and the precipitation figures diminished in the same order. The same authors⁵⁹ have prepared insoluble compounds by treating chromium sulphate with sulphuric acid. They have also investigated⁶⁰ the effects of flour, glucose, sodium acetate, sodium chloride, sodium sulphate, soluble starch, sulphonated castor oil, and sumach on the tanning properties and the precipitation figure of a chrome liquor. More chromium is adsorbed in presence of flour. D. Burton⁶¹ has shown that the amount of alkali necessary to start precipitation is increased by the addition of neutral salts. The increase is not proportional to the amount of added salt. According to R. E. Liesegang⁶² green solutions of chromium salts diffuse less quickly in gelatin, have a greater swelling effect, and a less tanning effect than violet solutions.

F. L. Seymour-Jones⁶³ has been unable to confirm F. C. Thompson and W. R. Atkin's theory⁶⁴ of the existence of a negatively charged colloidal complex in chrome tanning solutions. He has established its presence in some tanning liquors but not in all. E. Stiasny⁶⁵ has summarised a great deal of valuable information on judging the tanning value of chrome liquors. He discusses the constitution of some of the green and violet forms. The addition of neutral salts favours the formation of green salts.

⁵⁷ *J. Soc. Leather Trades Chem.*, 1923, **7**, 37; *J.*, 1923, 280A.

⁵⁸ *Ibid.*, 1923, **7**, 46; *J.*, 1923, 281A.

⁵⁹ *Ibid.*, 1923, **7**, 116; *J.*, 1923, 413A.

⁶⁰ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 372; *J.*, 1923, 900A.

⁶¹ *Ibid.*, 1923, **18**, 358; *J.*, 1923, 899A.

⁶² *Z. Leder- u. Gerb.-Chem.*, 1922, **2**, 90; *J.*, 1923, 511A.

⁶³ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 201; *cf. J.*, 1923, 367A.

⁶⁴ *Ann. Reptis.*, 1922, **7**, 356.

⁶⁵ *Collegium*, 1923, 95; *J.*, 1923, 733A.

Pelts should be tanned first with a liquor of high precipitation figure, and later one with a low precipitation figure should be used. Ageing affects the properties, the hydrolytic equilibrium and the colloidal character. The hydron concentration alters as the liquor stands, due to hydrolysis after dilution or to polymerisation of basic complexes.

ANALYSIS.

The most interesting work during the year has been in connexion with the analytical processes. Leather chemists are well aware that there is urgent need for improvements and a greater degree of concordance, but the present methods do not merit the scathing indictments which have been heaped upon them from several quarters. The attempts of J. A. Wilson and E. J. Kern⁶⁶ to supersede the official shake method of analysis of tanning extracts and materials have resulted in voluminous evidence, both analytical and fundamental, of the unique superiority of that method. The biennial conference of the Society of Leather Trades Chemists has adopted the methods of analysis of chrome leather recommended by the committee appointed to investigate that branch of work. This marks a new and welcome departure in the work of that Society. Hitherto the Society has confined its official regulations to tannin analysis. It is expected that official methods will be formulated at the next conference in 1924 for the analysis of lime liquors, chrome tanning liquors, and chrome and vegetable tanned leathers.

W. R. Atkin and A. Gardner⁶⁷ have proposed the use of tetrabromophenolsulphone-phthalein (Bromophenol Blue) as indicator in determining the temporary hardness of water.

Liming.

A committee of the Society of Leather Trades Chemists formed during the war has been actively at work during the last three years. The results have been very valuable. The first general report has been published during the year by F. C. Thompson.⁶⁸ It describes the objects and effects of liming and indicates what chemical properties and constituents of lime liquors may possibly influence these effects. The importance of the hydrogen-ion concentration on plumping and swelling is duly stressed and also its effect on the solvent action of the liquors. Determinations of the temperature, hydrogen ion concentration, caustic alkalinity, sulphides, and ammonia are considered to be the most important in controlling lime liquors. The methods of analysis have been

⁶⁶ *Ann. Repts.*, 1920, 5, 358.

⁶⁷ *J. Soc. Leather Trades Chem.*, 1923, 7, 87; *J.*, 1923, 372A.

⁶⁸ *Ibid.*, 1923, 7, 394; *J.*, 1923, 1084A.

entirely changed during the last ten years and fresh methods of analysis have been evolved for the determination of alkalinity, sulphides, amino-acids, and total alkalinity. These have been published in previous years. The sulphide determination has been revised again. W. R. Atkin⁶⁹ has applied the law of mass action and shown that the previous methods were theoretically unsound. In the new method 25 c.c. of the sulphide solution or lime liquor is added to 25 c.c. of a stock solution containing ammonia $N/2$ in strength, and also 12.5 grams of ammonium chloride per litre. The mixed solutions are then titrated with $M/20$ zinc sulphate solution, using lead acetate paper as external indicator. J. A. Wilson and A. F. Gallun, junr.,⁷⁰ have shown how to measure the plumping power of different solutions by means of pieces of calfskin and a thickness gauge.

Tannin Analysis.

This has been very fully reported on during the year and numerous investigations have been carried out to elucidate the best conditions for securing concordant results. A very frequent source of discrepancy in tannin analysis arises from the determination of the soluble matter. Filter candles and filter papers adsorb some of the dissolved matter. It is difficult to determine when a solution is " optically clear " as stipulated in the official method of tannin analysis, and when solutions which contain a large amount of insoluble matter are being filtered the pores of the filter paper or candle become lessened in size and filtration is changed into ultra-filtration. Recent experiments in the Procter International Research Laboratory, Leeds, have shown that it is possible to prepare membranes which will filter out any quantity of soluble matter from clear tannin solutions, and there is no doubt that this often occurs when tannin solutions are filtered for analytical purposes ; hence the discrepancies. F. C. Thompson⁷¹ suggests the determination of soluble tannins by the subsidence of the insoluble matter. The tannin infusion is poured into a glass cylinder about 5 cm. diameter to a height of exactly 20 cm. A mark is made on the wall of the cylinder exactly 5 cm. below the surface of the liquor. The solution is allowed to stand exactly 2 hrs., during which time the heavier insoluble particles settle out, leaving only very finely divided matter in suspension. 50 c.c. of the settled liquor is withdrawn from the liquor above the mark, and this is used for the determination of the soluble matter. This method obviates the errors due to different judgments on " optical clearness." Filtration, with its varied difficulties and uncer-

⁶⁹ *J. Soc. Leather Trades Chem.*, 1922, **6**, 427 ; *J.*, 1923, 152A.

⁷⁰ *Ind. Eng. Chem.*, 1923, **15**, 71 ; *J.*, 1923, 236A.

⁷¹ *J. Soc. Leather Trades Chem.*, 1922, **6**, 438 ; *J.*, 1923, 151A.

tainties, is dispensed with. The time involved is limited and there is no loss of time through slow filtration. There are differences between the results obtained by this method and those obtained by filtration, but these should not prejudice us against the new method. At present none of the insoluble matter which can be filtered out is classified as tans, whereas it is well known that insoluble matter can tan, and there is direct evidence to show that some of the material classified as insolubles is "tannin." L. Matrod⁷² has devised a special filtering apparatus including a Berkefeld filter candle. The candle is entirely surrounded by as small a quantity of liquor as 20 c.c., so that filtration is quicker and less liquor is wasted. P. Chambard, G. Hugonin, and Brun⁷³ have passed various criticisms on the official method of filtering tannin solutions. They have suggested that the insoluble matter should be determined by centrifuging the solutions for 10 min. in tubes 25 cm. long at 4000 revs. per min. The results obtained are much lower than those obtained with the filter candle; e.g., dry and liquid quebracho extracts yielded respectively 2.5% and 0.4% by centrifuging and 9.0% and 5.0% by the filter candle, presumably because very fine particles of suspended matter are not removed at the above speed. The Society of Leather Trades Chemists has not investigated these methods, but has compared filtration by filter paper and by filter candle, and it was decided at the recent conference⁷⁴ that tannin solutions must be filtered through a Berkefeld candle, and in order to avoid differences in the make and texture of the candle they must be procured from the same source, viz., A. Hough of Paris.

The official "shake" method of tannin analysis has been subjected to the usual crop of criticisms. G. Grasser⁷⁵ states that it gives very unreliable results, whereas the filter-bell method shows better concordance. A second detannisation of the tannin solution removes a further portion of "tans" and the "non-tans" are then colourless. This is the usual argument, and it is recognised that if "non-tannin" solutions are shaken with a fresh batch of hide powder the latter will adsorb some of the soluble matter, but it is not adsorbed under the conditions laid down by the official regulations, and it is not adsorbed in practice to any appreciable extent. L. Pollak⁷⁶ has replied to Grasser, and states that both methods are equally reliable for what they determine. Non-tan filtrates need not necessarily be colourless. He has used Grasser's own figures to prove his statements. R. J. Browne's work on

⁷² *J. Soc. Leather Trades Chem.*, 1923, 7, 167; *J.*, 1923, 510A.

⁷³ *Ibid.*, 1923, 7, 331; *J.*, 1923, 990A.

⁷⁴ *Ibid.*, 1923, 7, 521.

⁷⁵ *Z. Ledcr. u. Gerb.-Chem.*, 1922, 2, 20; *J.*, 1923, 319A.

⁷⁶ *Ibid.*, 1923, 2, 96; *J.*, 1923, 510A.

ultra-filtration⁵⁶ has dispelled a great deal of scepticism which has been caused by the attacks of Wilson and Kern.⁵³ G. W. Schultz⁷⁷ has conducted a series of experiments with purified gallotannic acid and hide powder from which he deduces that the official shake method is in error to the extent of 1·6%, whereas if a more concentrated solution was used, viz., 2·3 g. per 100 c.c., the error would be only 0·7%, which would amount to 0·2% of tannin in a 25% extract. W. Moeller⁷⁸ has criticised both the quantitative and qualitative methods of distinguishing tans from non-tans, and states that the properties of the different vegetable tannins are a function of the properties of the peptiser present in the tanning material.

Most valuable support for the official "shake" method of analysis has been forthcoming from a committee of the French section of the Society of Leather Trades Chemists,⁷⁹ which has decided in favour of filtration by the Berkefeld filter candle, rapid cooling of solutions, and detannisation with chromed hide powder. The work was continued⁸⁰ on six different extracts. All graduated glassware was calibrated, silver dishes were used for evaporation, freshly filled desiccators were employed, and only two dishes placed in each for cooling. A combined water-oven and water bath was used for evaporation, and the rapid weighing balances had a precision of 0·2 mg. The distilled water used was perfectly neutral and contained less than 0·003 g. of residue per 100 c.c. The kaolin was washed with acid and was neutral to phenolphthalein. Various tests are stipulated for the purity of the kaolin and the condition of the hide powder. The committee was of the opinion that still greater concordance could be obtained by more exactly defining the operations of chroming, washing, and weighing of the hide powder. Specific instructions were sent out to the members of the committee, and these were rigidly adhered to in some further analyses which were carried out.⁸¹ Liquid extracts were shaken in a machine until any deposit was intimately mixed with the rest of the sample. Pasty extracts were warmed in the water bath at 45° C., and then shaken. After shaking, the extract was cooled to 17°–18°, and sufficient weighed out to contain 3·75–4·25 g. of tannin. The extract was dissolved in 900 c.c. of distilled water at 85°–90°, cooled rapidly to 18°, made up to 1 litre and the analysis commenced at once. The hide powder was chromed for one hour with basic chromium chloride solution and allowed to stand overnight for at least one hour after shaking, then filtered and washed

⁵⁶ J. Amer. Leather Chem. Assoc., 1923, 18, 524; J., 1923, 1189A.

⁵⁷ Z. Leder- u. Gerb.-Chem., 1922, 2, 15; J., 1923, 319A.

⁵⁸ J. Soc. Leather Trades Chem., 1923, 7, 6; J., 1923, 280A.

⁵⁹ Ibid., 1923, 7, 212; J., 1923, 668A.

⁶⁰ Ibid., 1923, 7, 231; J., 1923, 668A.

LEATHER AND GLUE.

five times. The results were better but the non-tans did not agree too well. It was thought possible that the quantity of hide powder used was excessive, and that the p_{H_2} of the liquors should be adjusted. J. A. Wilson and E. J. Kern⁸² have observed that the p_{H_2} value affects the percentage of tannin as determined by the official "shake" method, but not as determined by their own method of tannin analysis. G. E. Knowles⁸³ and a committee of the British section of the Society of Leather Trades Chemists have been unable to discover much variation in the tannin analysis figures with various p_{H_2} values except in the case of the insolubles. The insolubles increase slightly with increased acidity and are more easily filtered off. Decreased p_{H_2} value coincides with increased flocculation of the insoluble matter.

Further detailed instructions are given in another report⁸⁴ from the French committee. Barks and woods should be ground in a Mussner mill until they pass through a 25-mesh sieve. Greer barks should be dried. Myrobalan nuts should be stoned and the two portions analysed separately. Valonia cups and beard should be separated for analysis. Dry extracts should be dried, weighed and powdered before analysis, and paste extracts also. Tannin infusions should contain 3·8-4·2 g. of tannin per litre, otherwise the amount of non-tannin adsorbed will vary. Crude materials should be extracted in a Procter extractor after having been soaked overnight. Five quantities of water (100-125 c.c.) at 50° C should be added to the extractor during one hour followed by boiling water until 1 litre of extract has been obtained. Concordant results were obtained by this means for sumach, quebracho wood, solid quebracho extract, and gambier paste, but not for chestnut wood and myrobalans. The committee advised more detailed specification of the type of mill, the extractor, the number of changes of water, the time of extraction, and the volume of water. J. Paessler and H. Sluyter⁸⁵ record a recent experience in which the discrepancies between the results from two analysts on a sample of sumach were due to one analyst extracting 2 litres whilst the other adhered to the official regulation of 1 litre. M. Auerbach⁸⁶ considers that the Koch extractor is not efficient, and suggests an entire revision of the official methods of tannin analysis.

The practical colour measurement of vegetable tan liquor has occupied the attention of several workers during the year. R. O. Phillips and L. R. Brown⁸⁷ give details for preparing and filtering

⁸² *J. Ind. Eng. Chem.*, 1922, 14, 1128; *J.*, 1923, 108A.

⁸³ *J. Soc. Leather Trades Chem.*, 1923, 7, 437; *Abs.*, 1924, B, 25.

⁸⁴ *Ibid.*, 1923, 7, 318; *J.*, 1923, 989A.

⁸⁵ *Collegium*, 1923, 245; *Abs.*, 1924, B, 26.

⁸⁶ *Ibid.*, 1923, 248; *Abs.*, 1924, B, 26.

⁸⁷ *J. Amer. Leather Chem. Assoc.*, 1923, 18, 24; *J.*, 1923, 152A.

tannin solutions previous to the measurement of the colour. Not more than 75 minutes should elapse from the time of dissolving to the time the tintometer reading is taken, as the solutions darken on standing and much more so if filtered. T. Blackadder⁸⁸ has evolved a method whereby each colour is measured separately. The depth of standard solution which passes half the light of the particular colour is measured in mm., hence the higher the readings the more transparent is the solution and the lighter coloured is the tanning material. H. R. Procter⁸⁹ has determined the half-light curve for a 20% iron alum solution, i.e., the depths of iron alum solution necessary to match half the colour at different parts of the spectrum transmitted through a spectroscope from a standard illuminant. Half-light curves for tannin solutions of analytical strength have also been obtained. Tannin solutions have been compared with the iron alum solution without a spectroscope but using ruby and copper-green glass screens respectively. The tannin solution is poured into the fixed cell and the iron alum solution in the adjustable cell. The method appears to be full of promise and obviates many of the difficulties attached to the Lovibond tintometer.

M. de la Bruère⁹⁰ has examined solutions of chestnut extract and quebracho extract, pure and in mixture, by the spectroscope in the ultra-violet region, and claims that it is possible to determine the proportion of each from the form of the absorption spectrum, but M. C. Lamb and V. C. W. Brown⁹¹ have been unable to confirm these claims.

A large amount of work has been carried out on leather analysis. L. Balderston⁹² considers that slicing is the best method of preparation, since each slice includes the whole thickness of the leather, the loss of moisture is slight, and there is less heating. The Society of Leather Trades Chemists favours sawing or grinding, although this must cause more heating, a greater loss in moisture, and more change in the grease contained.⁹³ The best method of determining the grease content has not been fixed yet. A. M. Hey⁹⁴ has shown that the presence of moisture in leather results in a greater amount of extract with both chloroform and petroleum spirit. G. W. Schultz⁹⁵ contends that oxidised and polymerised oils should not be included in the oils and grease extract, and if these are required

⁸⁸ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 194; *J.*, 1923, 668A.

⁸⁹ *J.*, 1923, 73T.

⁹⁰ *J. Soc. Leather Trades Chem.*, 1923, **7**, 121; *J.*, 1923, 413A.

⁹¹ *Ibid.*, 1923, **7**, 256; *J.*, 1923, 789A.

⁹² *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 154; *J.*, 1923, 511A.

Soc. Leather Trades Chem., 1923, **7**, 530.

bid., 1923, **7**, 385; *J.*, 1923, 65A.

bid., 1922, **6**, 389; *J.*, 1923, 65A.

then two extractions should be carried out, one with petroleum spirit and another with some suitable solvent for oxidised and polymerised products. L. Balderston⁹⁶ suggests petroleum spirit for the extraction and then the determination of the "fixed oil" by decomposing 5 g. of the extracted leather with alcoholic potash, acidifying, and extracting with petroleum spirit.

G. W. Schultz⁹⁷ disposes of the determination of water-soluble matter in a somewhat arbitrary manner by claiming that the excess tanning material extracted at 50° C., as compared with 4°, is adsorbed tannin and as such is part of the leather. The official method of determination includes a large percentage of adsorbed tannin, which imparts to the leather solidity and firmness. 30 g. of the leather should be extracted with 2 litres of water at 4° C. This temperature appears to be very arbitrary.

H. Rose⁹⁸ has compared the action of different accelerators in the Kjeldahl process. O. Gerngross and W. E. Schaefer⁹⁹ have worked out a micro-Kjeldahl method of determining nitrogen, which can be used on leather. G. Rehbein¹⁰⁰ has evolved a micro-Kjeldahl process.

The determination of free mineral acid in leather has claimed a good deal of attention during the year. S. Kohn and E. Crede¹⁰¹ propose an electrometric method in which the changes in the p_{H} value are noted of a water solution in equilibrium with the finely divided leather, following consecutive small additions of alkali. This method is claimed to prevent the reporting of synthetic tannins as free mineral acid. M. Jalade¹⁰² has modified the allowance for sulphur in the Balland and Maljean method, and has increased it to 0·36%, which is claimed to give better results. W. Moeller¹⁰³ describes the effect of the sulphonate group in synthetic tannins on leather, and M. Auerbach¹⁰⁴ has tried the effect of sulphuric acid on different leathers at different temperatures. C. van der Hoeven¹⁰⁵ has a new method for the determination of free sulphuric acid in leather. R. H. Pickard¹⁰⁶ has criticised leather analysis generally and the proposal of the British Boot, Shoe and Allied Trades Research Association to test for free mineral acid in leather by means of Thymol Blue paper.

⁹⁶ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 475; *J.*, 1923, 1084A.

⁹⁷ *Ibid.*, 1923, **18**, 254; *J.*, 1923, 734A.

⁹⁸ *Collegium*, 1923, 93; *J.*, 1923, 735A.

⁹⁹ *Ibid.*, 1923, 187; *J.*, 1923, 1107A.

¹⁰⁰ *Ibid.*, 1923, 256; *Abs.*, 1924, B, 26.

¹⁰¹ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 189; *J.*, 1923, 668A.

¹⁰² *J. Soc. Leather Trades Chem.*, 1923, 7, 129; *J.*, 1923, 413A.

¹⁰³ *Z. Leder- u. Gerb.-Chem.*, 1921, **1**, 303; *J.*, 1923, 108A.

¹⁰⁴ *Ibid.*, 1921, **1**, 227; *J.*, 1923, 108A.

¹⁰⁵ *Collegium*, 1922, 282; *J.*, 1923, 109A.

¹⁰⁶ *Chem. and Ind.*, 1923, 1213; *Leather Trades Rev.*, 1923, 944.

Chrome Leather and Tanning Liquors.

An official method has been passed by the Society of Leather Trades Chemists. The details have been given already.¹⁰⁷ An alteration has been made in the form of expression of the basicity.

A very important decision¹⁰⁸ is that regarding the form of expression of the basicity of chrome liquors. The present system leads to a good deal of confusion; the less basic a liquor, the greater is its basicity. The Schorlemmer method has been adopted, according to which the basicity figure is:—Amount of chromium combined with hydroxyl $\times 100 \div$ total chromium, i.e., the chromium present in excess of that required to satisfy the valencies of the acid in the salt Cr_2R_6 , expressed as a percentage on the total chromium. The following are examples:—

| | | Present method. | Above method. |
|---|-------|-----------------|---------------|
| $\text{Cr}_2(\text{SO}_4)_2$ | | 144 | 0 |
| $\text{Cr}_2(\text{OH})_2(\text{SO}_4)_2$ | | 96 | 33.3 |
| $\text{Cr}_2(\text{OH})_4\text{SO}_4$ | | 48 | 66.6 |
| $\text{Cr}_2(\text{OH})_6$ | | 0 | 100 |

The method of determination is quite simple. Instead of calculating the equivalence of the $N/2$ NaOH in terms of SO_4 , it is calculated to the equivalence of the SO_4 in terms of Cr assuming that the SO_4 was combined with Cr only (c.c. $N/2$ NaOH $\times 0.000865$ g. chromium required to saturate SO_4). This is divided by the total chromium and multiplied by 100.

K. Schorlemmer¹⁰⁹ has devised a method for determining the chromium and iron in waste chrome tanning liquors. L. Meunier and P. Chambard¹¹⁰ have made a very thorough study of the neutralisation of chrome leather and find that if the acid in the neutralising agent is weak, the whole of the combined sulphuric acid in the pelt can be converted into alkali sulphate. They have evolved a test for determining the acidity of the leather; 5g. of the finely divided leather is shaken with 50 c.c. of $N/5$ sodium bicarbonate and 50 c.c. of water for 3 hrs, then with a further 75 c.c. of water for 1 hr., finally with 50 c.c. for 1 hr., and the remaining sodium bicarbonate is determined. The method promises to be of great value in determining the basicity of the chrome salt on the fibre, but the leather should be first degreased and extracted with boiling water. L. Balderston¹¹¹ describes a method of analysing chrome leathers containing barium. W. R. Atkin and F. C. Thompson¹¹² suggest thymoiphthalein instead of phenolphthalein in the titration of two-bath chrome tanning liquors.

¹⁰⁷ *J. Soc. Leather Trades Chem.*, 1919, **3**, 194.

¹⁰⁸ *Ibid.*, 1923, **7**, 413; *Abs.*, 1924, B, 25.

¹⁰⁹ *Collegium*, 1922, 247; *J.*, 1923, 32A.

¹¹⁰ *J. Soc. Leather Trades Chem.*, 1923, **7**, 75; *J.*, 1923, 366A.

¹¹¹ *J. Amer. Leather Chem. Assoc.*, 1923, **18**, 491; *J.*, 1923, 1084A.

¹¹² *J. Soc. Leather Trades Chem.*, 1923, **7**, 50; *J.*, 1923, 281A.

F. P. Veitch, R. W. Frey, and I. D. Clarke¹¹³ have studied the wearing qualities of various shoe leathers in dry climates.

GLUE AND GELATIN.

Reference has been made above to the very valuable publications which have appeared on this subject. S. F. Sheppard and S. S. Sweet¹¹⁴ describe a plunger type of jelly strength tester. W. D. Richardson¹¹⁵ has described the Bloom gelometer for the same purpose. The plunger is fixed by a rigid bar to the under side of a pan attached by a hanger and an adjustable spring to a fixed bracket, and an electric device gradually increases the weight on the plunger until it sinks. R. de Izaguirre¹¹⁶ finds that the variation with time of the viscosity of gelatin solutions in the presence of increasing concentrations of hydrochloric acid shows a minimum with a maximum initial viscosity. Gelatinisation he considers is a dehydration and not a new chemical modification. J. Knaggs¹¹⁷ has determined the Hausmann numbers for diamino-acids of the proteins in gelatin. O. Gerngross and H. A. Brecht¹¹⁸ have studied the effect of hydrolysis of a 25% gelatin solution at p_{H} 4.7 at 100° C. and p_{H} 7.3 at 55° and 100°. The p_{H} increased with alkaline hydrolysis. The formaldehyde titration was difficult to perform after feeble hydrolysis and a new method is described. The authors have compared the diminution in solidity of the jelly with the increasing nitrogen figure. The decrease in viscosity and jelly strength with higher temperatures of hydrolysis has been confirmed. Viscosity and jelly strength are independent of each other. The adhesive power of a good gelatin is much greater than that of a technical glue of the same concentration. There is no simple relationship between hydrolysis, viscosity, jelly strength, and adhesive power. In all viscosity and jelly strength determinations, the hydron concentration should be noted, since the values are much lower at the isoelectric point than at the point of neutrality. The adhesive power does not depend so much on the p_{H} .

F. L. Seymour-Jones¹¹⁹ has contributed some studies on the formation of gelatin from hide powder by boiling it with water for varying periods of time. A process for manufacturing glue and gelatin from waste leather and ossein has been patented by J. Landau and E. Trepka.¹²⁰ Köln-Rottweil A.-G.¹²¹ have evolved

¹¹³ U.S. Dept. of Agric. Bull. 1168; J., 1923, 1142A.

¹¹⁴ Ind. Eng. Chem., 1923, 15, 571; J., 1923, 1189A.

¹¹⁵ Chem. and Met. Eng., 1923, 28, 551; J., 1923, 413A.

¹¹⁶ Anal. Fis. Quim., 1923, 21, 330; J., 1923, 1084A.

¹¹⁷ Biochem. J., 1923, 17, 488; J., 1923, 1084A.

¹¹⁸ Collegium, 1922, 262; J., 1923, 109A.

¹¹⁹ J. Soc. Leather Trades Chem., 1923, 7, 93; J., 1923, 367A.

¹²⁰ G.P. 365,448; J., 1923, 368A.

¹²¹ E.P. 203,276; J., 1923, 1085A.

another process in which split leather scrap^a and the like is decolorised with chlorine dioxide.

Simultaneous negative and positive adsorption of Bismarck Brown by gelatin and by leather powder has been discovered by M. A. Rakusin and G. T. Pekarskaja.¹²² S. C. Bradford¹²³ has a theory of gels according to which the setting of jellies is merely a process of crystallisation. A patent has been granted for purifying gelatin and glue.¹²⁴ E. Bateman and G. G. Town¹²⁵ have made comparative tests to show the diminution of the tensile strength of glue with increased hygroscopicity. R. E. Wilson and W. B. Ross¹²⁶ report that the gelling point of a glue can be raised by small additions of chrome alum. F. Lorenz¹²⁷ has worked out a method for determining the sizing colloids in glue.

¹²² *J. Russ. Phys.-Chem. Soc.*, 1916, **48**, 1889; *J.*, 1923, 41A.

¹²³ *Biochem. J.*, 1923, **17**, 230; *J.*, 1923, 735A.

¹²⁴ U.S.P. 1,457,466; *J.*, 1923, 735A.

¹²⁵ *Ind. Eng. Chem.*, 1923, **15**, 371; *J.*, 1923, 511A.

¹²⁶ *Ibid.*, 1923, **15**, 367; *J.*, 1923, 511A.

¹²⁷ *Papierfabr.*, 1923, **21**, 105; *J.*, 1923, 511A.

SOILS AND FERTILISERS.

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In this Report an attempt has been made to confine attention, as far as possible, to those aspects of the subject which represent the most noteworthy advances during the year on the practical and technical side. It will thus be found that many papers have been omitted from consideration either because they illustrate practical points which are already well known or of minor interest, or because their main interest at present lies in their theoretical aspects, and is thus more suitably dealt with in the writer's Report to the Chemical Society.

FERTILISERS.

One of the greatest difficulties encountered in the interpretation of the results of experiments designed to test the effect of fertilisers on crop production and the quality of crops, arises from the fact that, in addition to the effect of season, the efficiency of a fertiliser is greatly dependent on the nature of the soil and climatic conditions, and may thus vary enormously from place to place. The only way, therefore, to arrive at a reliable conclusion as to the practical value of a given fertiliser or class of fertiliser, is for the same experiment to be repeated for a number of years at a number of centres spread over the whole country, so as to embrace the most widely differing conditions of soil and climate. This system is now adopted at Rothamsted, and is well exemplified in the experiments on malting barley,¹ as well as in the experiments on ammonium chloride,² and on potash manures.³

Nitrogenous Fertilisers.

During the year under review there has been a steady increase in the consumption of nitrogenous fertilisers as compared with the previous year, the increase for sodium nitrate being estimated at about 25%, and that for ammonium sulphate at about 10%. The quantities available for the coming season will prove only just

¹ E. J. Russell, *J. Inst. Brew.*, 1923, **29**, 624; *J.*, 1923, 941A.

² See p. 412.

³ See p. 419.

sufficient to meet the world's requirements if present prospects of increased consumption are realised.

Synthetic Products.—A steady development is taking place in the industrial application of processes for the fixation of atmospheric nitrogen, and in the production of nitrogenous fertilisers thereby. In this country the plant at Billingham was expected to be in full commercial operation before the end of 1923. It will have a capacity of 100 tons of pure ammonia per day, capable of rapid expansion to 300 tons. In terms of ammonium sulphate these quantities correspond to 150,000 and 450,000 tons per annum.⁴ There has been a falling off in output of fixed nitrogen products in Germany in 1923, which will, however, doubtless be remedied on the establishment of more settled conditions. The growth of the German nitrogen industry is bound to have a powerful influence on German agriculture; the position in this connexion is dealt with in an article by F. Honcamp.⁵ Lively discussion has been aroused in France by the proposed agreement between the French Government and the Badische Anilin und Soda Fabrik whereby the sum of 5,000,000 francs would be paid to the latter for a concession to work the Haber process, which would be operated at Toulouse with a projected output of 36,000 tons of fixed nitrogen per annum. At present the whole French output of combined nitrogen from all sources is 19,000 tons annually, whereas the demand is about 110,000 tons. The relative values of the various nitrogen fixation processes have been examined in France by a special commission, which is understood to have reported that the Haber and Claude processes were about equally good, though under some circumstances the latter process had the advantage.⁶ This process⁷ is making good headway; it is in operation at Bethune,⁸ where coke-oven gas is used as a source of hydrogen,⁹ and a small plant is to be erected in Spain,¹⁰ while negotiations are in progress for factories in Belgium, Switzerland, and Italy.¹¹ In the latter country the Fauser process, which is similar in principle to the Claude Casale,¹² and Haber processes, is operating on a small scale.¹³ In the United States a good deal of attention is

⁴ *Chem. and Ind.*, 1923, 259.

⁵ F. Honcamp, *Z. Pflanz. Düng.*, 1923, 2, B, 147.

⁶ *Chem. and Ind.*, 1923, 228.

⁷ E.P. 171,972; *J.*, 1923, 54A. E.P. 171,970; *J.*, 1923, 95A. E.P. 177,777; *J.*, 1923, 656A.

⁸ *Chem. and Ind.*, 1923, 501.

⁹ *Comptes rend.*, 1923, 176, 394; *J.*, 1923, 266A.

¹⁰ *Chem. and Ind.*, 1923, 524.

¹¹ *Ibid.*, 1923, 752.

¹² U.S.P. 1,447,123; *J.*, 1923, 353A. E.P. 193,789; *J.*, 1923, 400A. E.P. 197,199; *J.*, 1923, 656A.

¹³ *Chem. and Ind.*, 1923, 835; *Giorn. Chim. Ind. Appl.*, 1923, 5, 171; *J.*, 1923, 601A.

being given to the possibility of reducing the cost of the cyanamide, cyanide,¹⁴ and synthetic ammonia¹⁵ processes.¹⁶ A process has also been patented for the production of oxides of nitrogen by the action of the streaming electric discharge on a mixture of oxygen and nitrogen,¹⁷ by which it is claimed that high yields are obtained. An account of the present position of the various processes in operation for nitrogen fixation has been given by E. K. Scott.¹⁸

Of more direct interest to the agricultural chemist is perhaps the question of the conversion of the primary products of nitrogen fixation (*i.e.*, ammonia oxides of nitrogen, cyanamide, and so on) into actual fertilisers. For the production of ammonium salts from ammonia two processes are now available, both of which offer considerable economic advantages over the use of free sulphuric acid. One of these¹⁹ consists in the use of synthetic ammonia in the Solvay ammonia-soda process, and the recovery of the by-product ammonium chloride. This process has now been successfully worked on the semi-large scale, the ammonium chloride being recovered by cooling the mother liquors from the sodium bicarbonate to 5°. It has also been found that sylvinitie can be used in the process instead of salt, thus giving a mixture of potassium and ammonium chlorides.²⁰ The alternative process consists in the production of ammonium sulphate by the interaction of ammonia and calcium sulphate.²¹ This is now being extensively used in Germany, obviating the need to make sulphuric acid, and utilising indigenous supplies of gypsum.

The production of urea from ammonia and carbon dioxide is now being worked on a semi-technical scale in the United States.²² The suitability of urea salts such as the nitrate or phosphate as fertilisers is now being investigated, and processes for the manufacture of these salts have been patented.²³ Attempts continue to be made to render calcium cyanamide suitable for use

¹⁴ U.S.P. 1,441,693; *J.*, 1923, 224A. U.S.P. 1,441,695; *J.*, 1923, 224A. U.S.P. 1,441,694; *J.*, 1923, 238A. E.P. 191,765; see also E.P. 192,791; *J.*, 1923, 353A. G.P. 364,589; *J.*, 1923, 353A. E.P. 194,026; *J.*, 1923, 451A. G.P. 370,152; *J.*, 1923, 499A.

¹⁵ See e.g. U.S.P. 1,465,310; *J.*, 1923, 1069A.

¹⁶ *Chem. and Met. Eng.*, Dec. 20, 1922; *Chem. and Ind.*, 1923, 80.

¹⁷ U.S.P. 1,458,525; *J.*, 1923, 929A.

¹⁸ *Chem. and Ind.*, 1923, 498.

¹⁹ E.P. 130,365, 131,870; *J.*, 1919, 690A; 1920, 266A.

²⁰ G. Claude, *Comptes rend.*, 1923, 177, 782; *J.*, 1923, 1191A. See also *Chem. and Ind.*, 1923, 1108.

²¹ *Chem. and Ind.*, 1923, 435.

²² See ¹⁵. For the French process see J. L. M. Frejacques, F.P. 527,733.

²³ E.P. 179,544; *J.*, 1923, 901A. E.P. 182,134; *J.*, 1923, 1037A. U.S.P. 1,440,056; *J.*, 1923, 683A.

directly as a fertiliser,²⁴ but except possibly as a constituent of mixed manures its future in this direction is not hopeful.

Natural Products.—The slump of 1921 in the Chilean nitrate industry now seems to have been successfully left behind, and exports have increased considerably.²⁵ The price has been very stable, having fluctuated only between £11 7s. 6d. and £13 per ton. J. Stoklasa²⁶ has put forward a general theory of 'the volcanic origin of the Chile deposits, and attributes the alleged superiority of Chilean nitrate over chemically pure or synthetic nitrate for sugar beet—of which superiority the present writer knows of no satisfactory evidence—to its radioactivity, with its iodine content as a secondary factor. In South Africa an underground store of nitrate-bearing brine has been discovered at Matsap Pan, containing $4\frac{1}{2}$ tons of nitrate (mostly of sodium) per 100,000 gallons.²⁷ Chinese deposits of saltpetre-bearing earth are now being worked, 2000 tons of pure salts being produced annually.²⁸

The European production of by-product ammonium sulphate shows an increase of about 50,000 in 1923 compared with the previous year, while the output in the United States has not changed materially. Prices in Great Britain have been steady at about £14 15s. per ton.

A German summary of the literature on the use of crude gas liquor as a fertiliser has appeared.²⁹ In pot experiments it was found that the harmful effects of the toxic constituents of the liquor disappeared within eight days.

• *The Relative Efficiency of Nitrogenous Fertilisers.*

During the year the results of a number of experiments on the relative manurial value of various nitrogenous fertilisers have been published.

Sodium nitrate is in general between 5 and 10% more effective than ammonium sulphate; this relation is confirmed by the results of W. Schneidewind and F. Munter³⁰ in field experiments, and of A. Thomson^{30A} in water culture, and it is reflected in the terms of an agreement in Germany between the farmers, the nitrogen

²⁴ E.P. 174,599; *J.*, 1923, 282A. G.P. 379,418; *J.*, 1923, 1191A. G.P. 376,420; *J.*, 1923, 901A. G.P. 362,448; *J.*, 1923, 154A.

²⁵ *Chem. and Ind.*, 1923, 818.

²⁶ *Comptes rend.*, 1923, 176, 1570; *J.*, 1923, 715A.

²⁷ *S. Afr. J. Ind.*, Feb., 1923; *Chem. and Ind.*, 1923, 350.

²⁸ *Chem. and Ind.*, 1923, 155.

²⁹ *Gas u. Wasserfach*, 1923, 66, 25; *J.*, 1923, 194A.

³⁰ W. Schneidewind and F. Munter, *Abh. Deut. Landw. Ges.*, 1923, No. 324 (36 pp.).

^{30A} A. Thomson, *Acta et Commentationes Univ. Dorpatensis*, 1922, A3, (2); *J.*, 1923, 1036A.

industry, and the government,³¹ whereby the price of nitrogen in the form of sodium nitrate is fixed at ten-ninths of that of the nitrogen in ammonium sulphate. This difference may have its cause partly in the fact that ammonium sulphate is liable to suffer a loss of ammonia when applied to alkaline soils before or at the time of seeding, but this is less liable to occur if applied as a top dressing. This has been shown to be particularly the case in Egyptian soils by J. A. Prescott.³² It must also be remembered that ammonium sulphate is "physiologically acid" fertiliser, leaving an acid residue in the soil, and thus tending to cause sourness, or to accentuate the sourness of an already sour soil, to the detriment of some crops. Sodium nitrate, on the other hand, is "physiologically alkaline." Crops specially suited to moderately acid conditions, such as the potato, may, however, do better with ammonium sulphate; further, there is evidence that iron is more readily available under the conditions of increased hydrogen-ion concentration set up by ammonium sulphate.³³ The inferiority of nitrate to ammonium salts as manures for rice is ascribed to this effect by L. G. Willis and J. O. Carrero,³⁴ the alkaline residue from sodium or calcium nitrate rendering the iron less available and thus setting up chlorosis.

Experiments on the relative value of calcium cyanamide ("nitrolim") and ammonium sulphate have been carried out in the field by W. Schneidewind and F. Munter,³⁵ and in pots by E. Haselhoff, O. Liehr, and K. Fluhrrer.³⁶ The results of both sets of experiments agree in giving calcium cyanamide a much lower value than that of ammonium sulphate; they also bring out the very great uncertainty in the effect of cyanamide, results even superior to those given by ammonium sulphate being sometimes obtained; whereas in other cases the crop is actually depressed below that given when no nitrogen at all is applied. It is already known from the work of Cowie³⁶ that dicyanodiamide, the presence of which in calcium cyanamide is liable to give rise to harmful effects, is only decomposed with extreme slowness in the soil, and that its deleterious action depends partly on its power of inhibiting the action of the nitrifying organisms. R. V. Norris, B. Viswanath, and C. U. R. Ayyer³⁷ have shown that although in moderate doses there is no conversion of cyanamide to dicyanodiamide in the soil, such conversion does occur if the concentration of cyanamide is high. It seems very probable that many of the unfavourable

³¹ *Chem. and Ind.*, 1923, 1200.

³² *J. Agric. Sci.*, 1923, **13**, 333; *J.*, 1923, 847A.

³³ H. Jones and W. Shive, *Ann. Bot.*, 1923, **37**, 355.

³⁴ *J. Agric. Res.*, 1923, **24**, 621; *J.*, 1923, 1036A.

³⁵ *Landw. Vers.-Stat.*, 1922, **100**, 37.

³⁶ G. A. Cowie, *J. Agric. Sci.*, 1919, **9**, 113; 1920, **10**.

³⁷ *Mem. Dept. Agric. India Chem. Ser.*, 1923, **7**, 55.

results which have been obtained in the use of nitrolim may be due to bad distribution, resulting in local regions of high concentration favourable to the production of dicyanodiamide.

Comparisons of ammonium sulphate with ammonium chloride and urea have been made at Rothamsted and a number of outside centres,³⁸ and by W. Schneidewind and F. Munter³⁹ and E. Haselhoff, O. Liehr, and K. Fluhrer.³⁵ All these experiments agreed in showing that on the average the two ammonium salts were about equally effective. With regard to urea, the Rothamsted experiments indicated that it was, if anything, somewhat superior to ammonium sulphate, though less effective than sodium nitrate. In the German experiments, however, both urea and urea nitrate were on the average only about 85% as effective as ammonium sulphate.

Ammonium bicarbonate³⁹ has been tested in Germany by E. Haselhoff, O. Liehr, and K. Fluhrer,³⁵ and by O. Lemmermann and K. Eckl.⁴⁰ The results indicate that this salt may be, under certain circumstances (*e.g.*, when applied before sowing and harrowed in immediately), as effective as ammonium sulphate; but if applied as a top dressing, as would be expected, marked losses of ammonia occur, and the crop increase is less.

Leguminous crops are commonly grown without special nitrogenous manuring. There is, however, some evidence that such manuring may be of value, especially in the early stages of the growth of the plant, before nodule formation is far advanced. Results of experiments on the nitrogenous manuring of clover have been published by Kuhnert,⁴¹ and the subject has been discussed by L. Hiltner.⁴²

The special effect of nitrogenous fertilisers in stimulating vegetative growth and leaf production, as opposed to maturation and ripening, is well illustrated by the work of L. Blaringhem,⁴³ who has studied the effect of the common fertilisers on the anatomy and development of seedlings of various plants.

Analysis.—Without going into details, reference may be made to papers by G. H. Buchanan,⁴⁴ E. J. Fox and W. J. Geldard,⁴⁵ A. Grammont,⁴⁶ A. Nanussi,⁴⁷ and W. Wagner⁴⁸ on the analysis of cyanamide and its products of hydrolysis, and to a paper by

³⁸ Rothamsted Experimental Station Report for 1921-22, p. 16.

³⁹ See *Ann. Repts.*, 1922, 7.

⁴⁰ *Z. Pflanz. Dünig.*, 1923, 2, B, 98.

⁴¹ *Ibid.*, 1923, 2, B, 137.

⁴² *Ibid.*, 1923, 2, B, 253.

⁴³ *Comptes rend.*, 1923, 177, 407; *J.*, 1923, 941A.

⁴⁴ *Ind. Eng. Chem.*, 1923, 15, 637; *J.*, 1923, 798A.

⁴⁵ *Ibid.*, 1923, 15, 743; *J.*, 1923, 901A.

⁴⁶ *Bull. Soc. Chim.*, 1923, 33, 123; *J.*, 1923, 281A.

⁴⁷ *Giorn. Chim. Ind. Appl.*, 1923, 5, 168; *J.*, 1923, 618A.

⁴⁸ *Z. angew. Chem.*, 1923, 36, 19; *J.*, 1923, 154A.

J. Bordas⁴⁹ on the Jodlbauer method for the determination of nitrogen.

Phosphatic Fertilisers.

The supply of phosphorus to the growing crop depends on factors not entirely comparable with those relating to the supply of nitrogen and potassium, and this difference has an important bearing on the question of the use of phosphatic fertilisers. Potash occurs plentifully in nature in soluble forms, as in the Stassfurt and Alsatian deposits which form the main sources of potash fertilisers. Soluble nitrogenous compounds are available both as natural deposits and as the products of industrial processes, and the nitrogen in insoluble compounds is of value as a fertiliser only in so far as it becomes soluble and available to the plant under the influence of soil micro-organisms. Phosphorus, on the other hand, occurs almost wholly as insoluble phosphates, in the form of bones and of natural deposits; whereas in general it is found that the most effective phosphatic fertilisers are those compounds in which the phosphate is readily soluble in water or in weakly acid solvents. In the past this difficulty has been met either by the conversion of raw phosphates into superphosphate by means of sulphuric acid, or by the use of basic slag. The supply of the latter material, and its suitability for agricultural use, are dependent on factors which are outside the control of the agriculturist, and at the present time the supply of slag of suitable quality is insufficient.

The manufacture of superphosphate is, relatively speaking, an expensive process, with the result that superphosphate manufactured from imported raw phosphates in countries such as our own labours under a considerable economic disadvantage in competition with that made in continental countries possessing their own supply of raw phosphates, and with somewhat depressed exchanges. Still worse is the position of Germany and other central European States whose exchanges are so low that they are entirely unable to import raw phosphates for superphosphate manufacture. The upshot is that more and more attention is being given to the possibility of developing alternative methods for utilising insoluble phosphate, whether of high grade such as now are used for making superphosphate, or of too low a grade for such use. In Germany in recent years attempts have even been made to maintain that phosphatic manuring can be dispensed with, but the fallacy of such arguments appears to have been realised in many quarters in Germany to-day, and more attention is being given to the diagnosis of phosphate deficiency in soils so as to insure the most economical use of phosphatic fertilisers.

Basic Slag.—Basic slag of high citric-solubility, whether it be of high or of moderately low grade, is an article of established value

⁴⁹ *Comptes rend.*, 1923, 177, 696; *J.*, 1923, 1190A.

for which a ready market can always be found. Unfortunately, a large part of the basic slag produced by the steel works in this country is of very low grade, and usually, owing to the use of fluorspar, also of low solubility. Such material is difficult to dispose of at fair prices. D. N. McArthur⁵⁰ has directed attention to the possible value of such slags as a source of lime for the land. An alternative outlet for slags of this type might be their treatment by a process patented in Germany⁵¹ for the extraction of phosphates from basic slag by fusion with potassium chloride or other alkali chloride. The whole of the phosphate is stated to be present in the clear melt, leaving the lime in the residue.

Raw Phosphates and their Utilisation.—Some idea of the magnitude of the European demand for raw phosphates is given by the figures for 1913, when 4,413,000 tons was consumed for all purposes; of this more than half came from North Africa, over one-third from the United States, and about one-tenth from France and Belgium. Most of the North African phosphates come from Tunis and Algeria at present, but there are also large deposits in other parts of North Africa, notably in Morocco, where the output has risen from 8230 tons in 1921, to 85,583 tons in 1922. It is hoped by 1927 to reach an output from Morocco of over one million tons, while that from Algeria and Tunis is expected to reach 3½-4 million tons.⁵² The output from Nauru and Ocean Islands in the Pacific, in 1922-3, was 361,205 tons, practically the same as the previous year; the greater part of this was consumed in the Antipodes, only some 4·5% finding its way to this country.^{53, 54} Extensive phosphate deposits, mostly of low grade, exist in Russia.⁵⁵

Raw phosphate is used mainly for the manufacture of superphosphate. A number of other methods for treating raw phosphates in order to increase their solubility have been proposed. Some of these still depend on the use of acids. For example, F. Kanhäuser describes a process in which the amount of sulphuric acid used is less than that needed to produce superphosphate; it is stated that by this means carbonates and fluorides are decomposed and thus prevented from exerting a deterrent action on the solubility of the phosphates.⁵⁶ When raw phosphates are decomposed by means of nitric acid, and ammonia is passed into the acid liquors in bulk, the resulting phosphate precipitate is of low citric-solubility. By feeding the acid liquors and ammonia together into a mixing chamber, and removing the product con-

⁵⁰ *J.*, 1923, 213T.

⁵¹ G.P. 362,989; *J.*, 1923, 194A.

⁵² *Chem. and Ind.*, 1923, 521.

⁵³ *Ibid.*, 1923, 438.

⁵⁴ *Ibid.*, 1923, 1041.

⁵⁵ *Z. Pflanz. Düng.*, 1923, 2, B, 315.

⁵⁶ *Chem.-Zeit.*, 1923, 47, 121; *J.*, 1923, 281A.

tinuously, it is claimed that this difficulty may be overcome, and a product of high citric-solubility obtained.⁵⁷ The same difficulty is liable to arise when superphosphate is neutralised by ammonia, but C. Matignon⁵⁸ has now described a process, depending on the use of dilute gaseous ammonia (3-5%) for the neutralisation, which results in a product containing three-quarters of its phosphate in a water-soluble condition. In the manufacture of this product, to which the name "Superam" has been given, the amount of sulphuric acid used is only 48% of that which would be needed in making a mixture of sulphate of ammonia and superphosphate containing the same amount of nitrogen and phosphate. The "Rhenania" process for the treatment of raw phosphates⁵⁹ and other similar processes⁶⁰ depend on the incineration of a mixture of the raw phosphate with silicious materials, resulting in products with high citric-solubility. The Bureau of Soils of the U.S. Department of Agriculture is working on a process which goes a stage further than this, and actually volatilises the phosphoric oxide from low-grade rock in admixture with sand and coke.⁶¹ The phosphoric acid produced could be utilised for the production of soluble neutral phosphates, e.g., of alkalis or ammonium, or it can be used to act on a further quantity of rock to give so-called "double superphosphate."⁶² Other processes depend on the heating of raw phosphate with alkali salts, either with⁶³ or without⁶⁴ the addition of carbonaceous material.

As an alternative to chemical treatment, raw phosphates may be reduced physically to an extremely fine state of subdivision. This may be effected in the Plauson mill, using silicates, alkalis, or organic protective colloids to aid dispersion and to prevent re-aggregation of the finer particles,⁶⁵ but it is at least doubtful whether this process will prove sound economically. In Morocco a small-scale plant is being worked for the grading of ground phosphate rock by an air current, the finest material being recovered in a Cottrell precipitation plant.⁶⁶

The Relative Efficiency of Phosphatic Fertilisers.—Perhaps no other class of manures is liable to give such conflicting results in field trials as are obtained with phosphatic fertilisers. Not only

⁵⁷ G.P. 363,272; *J.*, 1923, 194A.

⁵⁸ *Chim. et Ind.*, 1923, **10**, 1216; *J.*, 1923, 1037A.

⁵⁹ E.P. 174,370, 177,496; *J.*, 1923, 24A. See also *Ann. Repts.*, 1922, **7**, 370. P. Krische, *Z. angew. Chem.*, 1923, **36**, 130; *J.*, 1923, 321A.

⁶⁰ E.P. 194,208; *J.*, 1923, 466A; *Chem. and Ind.*, 1923, 1108.

⁶¹ W. H. Waggoner, *J. Amer. Soc. Agron.*, 1923, **15**, 152; W. H. Ross and A. R. Merz, *Chem. and Met. Eng.*, 1923, **29**, 313.

⁶² U.S.P. 1,470,968; *J.*, 1923, 1191A.

⁶³ U.S.P. 1,437,450; *J.*, 1923, 111A.

⁶⁴ E.P. 191,129; *J.*, 1923, 194A.

⁶⁵ E.P. 195,655; *J.*, 1923, 512A.

⁶⁶ *Chem. and Ind.*, 1923, 1108.

do agricultural crops differ markedly in their response to phosphatic manuring, but the type of soil and the climate exert a large effect on the result. It is now well established that the more insoluble phosphates, such as ground rock phosphate or bone manures, are most effective on sour soils and under moist conditions. These conditions are, however, much less favourable to the action of superphosphate, which acts best on dry, calcareous soils, on which insoluble phosphates usually give disappointing results. It is possible to put forward an interpretation of these differences in terms of soil factors, which, while not covering the whole ground, certainly accounts for most of the observed facts.

Sour soils, besides being acid in the chemical sense, contain, in virtue of that acidity, soluble iron and aluminium salts. On the application of water-soluble phosphates, such as superphosphate, to such soils, a considerable proportion of the phosphate is precipitated in the form of insoluble phosphates of iron and aluminium, which are not readily available to the plant, and the extent of this "reversion" increases gradually with time. On an alkaline, calcareous soil, however, the interaction of the soluble phosphate with the calcium bicarbonate in the soil solution and with the adsorbed calcium ions on the colloidal surface of the soil particles gives a finely divided precipitate of dicalcium phosphate which is comparatively easily soluble in water saturated with carbon dioxide. The natural rock and bone phosphates, however, consist of tricalcium phosphate combined with excess of lime, are in a relatively coarse condition, and are only slightly soluble in carbonic acid solutions; hence they are less effective in non-acid soils than in sour soils with an acid soil solution. The case of basic phosphates such as basic slag (made without the use of fluorspar) and such products as Rhenania phosphate—the phosphoric acid of which, although insoluble in water, is soluble in weak acids—differs from that of raw mineral phosphates. There is reason to believe that much of the phosphoric acid in such phosphates exists in the form of silicophosphates having an appreciable solubility even under faintly alkaline conditions, thus explaining the superiority of such fertilisers over raw phosphates on many non-acid soils. The papers by A. Demolon,⁶⁷ A. Demolon and P. Boisshot,⁶⁸ C. Brioux,⁶⁹ P. L. Gile and J. O. Carrero,⁷⁰ and T. D. Hall and J. C. Vogel⁷¹ should be consulted in this connexion.

The favourable action of acid conditions on the availability of ground rock phosphate has led to the advocacy of the use of

⁶⁷ *Ann. Sci. Agron.*, 1923, **40**, 151.

⁶⁸ *Comptes rend.*, 1923, **176**, 777; *J.*, 1923, 414A.

⁶⁹ *Comptes rend.*, 1922, **175**, 1096; *J.*, 1923, 110A; *Ann. Sci. Agron.*, 1923, **40**, 185.

⁷⁰ *J. Agric. Res.*, 1923, **25**, 171; *J.*, 1923, 1190A.

⁷¹ *Soil Sci.*, 1923, **15**, 367; *J.*, 1923, 847A.

physiologically acid fertilisers,⁷² such as ammonium sulphate, in conjunction with raw phosphates. This idea was put forward over twenty years ago in Russia by Prjanischnikow.^{55, 73} It has recently been actively supported in Germany by M. von Wrangell, and forms the basis of a system of phosphatic manuring⁷⁴ which has, however, given rise to considerable discussion,⁷⁵ partly of a rather acrimonious nature. The obvious drawback to such a system is that it could only be successfully applied to soils with little or no reserve of lime, and on these soils it might do more harm than good by hastening the production of toxic concentrations of acid in the soil.⁷⁶

The results of several vegetation experiments on the comparison of different phosphatic fertilisers have been published during the year, of which mention may be made of the Rothamsted experiments,⁷⁷ those of W. Schneidewind and F. Munter,⁷⁸ and those of G. S. Robertson⁷⁹ on the turnip crop in North Ireland. In the latter experiments Gafsa phosphate, high grade basic slag, and a Belgian product known as "Peerless basic phosphate," all gave as good a result as superphosphate, although Nauru phosphate was not quite so effective. The Belgian product is apparently of the same nature as "Rhenania" phosphate,⁷⁹ further trials of which have been carried out in Germany⁸⁰ with quite favourable results. The effects of the American product, "Ammo-Phos"⁸¹ on germination have been studied by D. G. Coe.⁸² A. W. Oldershaw's well-known experiments at Saxmundham have been summarised⁸³ up to 1922.

Finally, mention may be made of an interesting point in connexion with the use of phosphatic manures on warm early soils.

⁷² See p. 411.

⁷³ D. N. Prjanischnikow, "Die Düngerlehre," (Berlin, P. Parey, 1923), p. 283.

⁷⁴ M. von Wrangell, *Landw. Vers.-Stat.*, 1920, 98, 1; *Landw. Jahrb.*, 1922, 57, 50; "Phosphorsäureaufnahme und Bodenreaktion" (Berlin, Parey), 1920; Aereboe, "Neue Düngewirtschaft ohne Auslandsphosphate," 1922.

⁷⁵ P. Ehrenberg, *Z. Pflanz. Düng.*, 1923, 2 B, 73, 411; M. von Wrangell, *ibid.*, 408; O. Lemmermann, *ibid.*, 419; O. Lemmermann, E. Haselhoff, and T. Pfeiffer, E. A. Mitscherlich, J. Hasenbäumer, and O. Nolte, "Die Phosphorsäure-Frage" (Verlag Chemie, Leipzig), 1922.

⁷⁶ P. Ehrenberg, *Z. Pflanz. Düng.*, 1923, 2, B, 129. See also F. Munter, *ibid.*, 497.

⁷⁷ *Rothamsted Expt. Sta. Report*, 1921-22, p. 17.

⁷⁸ "Phosphates and Improvements of Pasture," Government of Northern Ireland, Min. of Agr., p. 9 (1923).

⁷⁹ See p. 415.

⁸⁰ E. Haselhoff and O. Liehr, *Landw. Vers.-Stat.*, 1922, 100, 21. T. Remy and Weiske, *Landw. Jahrb.*, 1923, 59, 203. A. Gehring and E. Pommer, *Z. Pflanz. Düng.*, 1923, 2, B, 404.

⁸¹ See *Ann. Repts.*, 1922, 7, 363.

⁸² *New Jersey Agr. Expt. Station Bull.* 375, 1923.

⁸³ *J. Min. Agric.*, 1923, 30, 308.

The effect of phosphates in accelerating ripening of cereals is of great value in backward districts, but in early districts it may easily become a disadvantage, since in such districts in a normal season the crop already tends to ripen off before it has made its maximum possible growth. Such an instance occurred in an experiment on light sandy soil in Suffolk in 1922, where the yield of barley was lower on the plot receiving phosphate than it was on that receiving none.⁸⁴ This affords an excellent illustration of the manner in which the effect of fertilisers may be influenced by environmental factors.

The Evaluation of Phosphatic Fertilisers.—The value of the determination of the citric-solubility of the phosphate in basic phosphatic manures, and more particularly in basic slags, by the official method is rather a vexed question. Although cases do arise in which basic slags of low citric-solubility are as effective in the field as those of high solubility, there are still grounds for maintaining that the citric-solubility of basic slag is of use in assessing the value of the slag as a fertiliser. In view of the influence of soil and climatic conditions on the effect of fertilisers, and particularly of phosphatic fertilisers, as instanced on p. 416, it is still manifestly impossible to devise any laboratory test which will assess the value of a slag under all conditions of soil and climate. All that can be asked of such a laboratory test is that it shall furnish the expert with data from which he can decide as to the probable value of the fertiliser under specified conditions of soil and climate. Judged from this standpoint, the official citric-solubility test, though far from perfect, is nevertheless a useful one.

H. R. Christensen⁸⁵ has carried out a comprehensive investigation on the solubility of raw mineral phosphates, various prepared basic phosphates, and basic slag, in 2% citric acid⁸⁶ and in some of the other solvents that have been suggested, such as ammonium citrate and water saturated with carbon dioxide,⁸⁷ and has compared the results with those obtained by a biological method depending on the ability of the tested material to supply soluble phosphate, under faintly alkaline conditions, in sufficient amount to enable a culture of *Azotobacter* to make a vigorous growth. In general, the results of the biological test are in better accord with what is known as to the relative value of phosphates of the type tested, on non-acid soils, than are the results of the chemical solubility tests. G. S. Robertson and

⁸⁴ *J. Min. Agric.*, 1923, **29**, 945.

⁸⁵ *Tidsskr. for Planteavl.*, 1923, **29**, 513, with English summary at end.

⁸⁶ See also H. F. L. Bischoff and B. de C. Marchand, *J. S. Afr. Chem. Inst.*, 1923, **6**, 53.

⁸⁷ See also Maschhaupt, *Versl. Landbouwk. Onderz. Rijkslandbouw-proefstat.*, 1922; *J.*, 1923, 110A.

F. Dickinson⁸⁸ have proposed a modification of the official citric-solubility test, based on the use of one gram of material instead of five. A method for the determination of free phosphoric acid in superphosphate has been patented.⁸⁹ Sources of error in the determination of insoluble phosphates have been discussed by W. R. Austin.⁹⁰

Potash Fertilisers.

Sources of Potash.—The imports of potash salts from Germany into this country showed a steady and considerable increase between 1920 and 1922.⁹¹ The world's consumption of potash in the latter year is estimated at 1,600,000 tons, of which Germany supplied 1,300,000 tons.⁹² Alsatian competition, which was thus not much felt in 1922, began to have a decided influence in 1923, during the first nine months of which roughly 200,000 metric tons less German potash was sold.⁹³ This is reflected in the increased output of the Alsatian mines, which reached over 1,300,000 tons in 1922, the highest figure since the mines were taken over by France.⁹⁴ The extensive leucite deposits in Italy, estimated to exceed a thousand million tons, are now being worked. The iron is separated magnetically, and the remaining mineral, with a potash content of 21.5%, is said to be as effective as potassium sulphate as a fertiliser.⁹⁵ The discovery of large deposits of potash is also reported from Czechoslovakia.⁹⁶ The manufacture of potassium salts from kelp is described by J. W. Turrentine, H. G. Tanner, and P. S. Shoaff.⁹⁷ The recovery of potash from distillery waste forms the subject of a United States patent.⁹⁸

The Relative Value of Potash Fertilisers.—The main interest in the use of potash fertilisers centres in the relative value of the high-grade sulphate and chloride, and the low-grade salts such as kainite and sylvinit. Trials on this subject are in progress at Rothamsted and a number of other centres. The results of the 1922 experiments⁹⁹ indicated that the high-grade salts, whether sulphate or chloride, were equally effective as regards their influence on the

⁸⁸ *J.*, 1923, 59T.

⁸⁹ U.S.P. 1,462,840; *J.*, 1923, 941A.

⁹⁰ *Ind. Eng. Chem.*, 1923, 15, 1037; *J.*, 1923, 1143A.

⁹¹ *Chem. and Ind.*, 1923, 405.

⁹² *Ibid.*, 1923, 684.

⁹³ *Ibid.*, 1923, 1091.

⁹⁴ U.S. *Comm. Rep.*, April 9, 1923; *Chem. and Ind.*, 1923, 523. For an account of the present position of the French potash industry see M. Mennecke, *Fert. and Feeding St. J.*, 1923, 8, 602.

⁹⁵ *Chem. and Ind.*, 1923, 1126, 1133.

⁹⁶ *Cham. Com. J.*, Sept. 14, 1923; *Chem. and Ind.*, 1923, 1061.

⁹⁷ *Ind. Eng. Chem.*, 1923, 15, 159; *J.*, 1923, 306A.

⁹⁸ U.S.P. 1,444,833; *J.*, 1923, 323A.

⁹⁹ *Rothamsted Expt. Sta. Report*, 1921-22, pp. 18, 21. See also *J. Min. Agr.*, 1923, 29, 947.

yield of potatoes, but that the low-grade salts gave diminished yields. When quality was taken into consideration, the inferiority of the latter salts was still more marked, and even the high-grade chloride gave potatoes of a somewhat inferior quality to those given by the sulphate. Similar results are reported by O. Lemmermann and K. Eckl,¹⁰⁰ and by W. Schneidewind and F. Munter,²⁹ who found, however, that for rye the low-grade salts and the high-grade were equally effective. F. W. Morse¹⁰¹ could find no significant difference between the effect on the soil of continued use of potassium chloride or sulphate; contrary to what might have been expected, there was no evidence for a more rapid loss of lime by the use of the former.

The special part played by potash in the nutrition of the plant is well brought out by the experiments of H. Wiessmann,¹⁰² which, besides confirming most of the well-known effects of potash on plant growth, illustrated clearly the fact that under conditions of potash-starvation plants fail to reach maturity, whereas shortage of nitrogen or phosphate, although inducing stunted growth, does not prevent the plants from flowering and setting seed. The influence of potash manuring on the intake of phosphate by various crops has been studied by O. Nolte,¹⁰³ who showed that lack of available phosphate in the soil could not be counteracted by plentiful manuring with potash.

Analysis.—The perchlorate and cobaltinitrite methods for the determination of potassium have been investigated by R. L. Morris.¹⁰⁴ The latter method has also been studied by E. Cleyfert.¹⁰⁵ A further modification of the volumetric bitartrate method of Przibylla¹⁰⁶ has been described by P. Hubert.¹⁰⁷ N. E. Gordon has pointed out certain sources of error in the determination of potash in mixed fertilisers.¹⁰⁸

Organic and Mixed Manures.

Two matters call for special mention under this heading.

The use of town refuse for manurial purposes is spreading in this country.¹⁰⁹ In Italy extensive use is made of the Beccari

¹⁰⁰ *Z. Pflanz. Düng.*, 1923, **2**, B, 385.

¹⁰¹ *Soil. Sci.*, 1923, **16**, 107; *J.*, 1923, 1143A.

¹⁰² *Z. Pflanz. Düng.*, 1923, **2**, A, 1; *J.*, 1923, 566A.

¹⁰³ *Ibid.*, 1923, **2**, B, 23; *J.*, 1923, 566A.

¹⁰⁴ *Analyst*, 1923, **48**, 250; *J.*, 1923, 1000A.

¹⁰⁵ *Bull. Soc. Chim. Belg.*, 1922, **31**, 417; *J.*, 1923, 164A. See also Pozzi-Escot, *ibid.*, 1923, **32**, 227.

¹⁰⁶ See *Ann. Repts.*, 1922, **7**, 272.

¹⁰⁷ *Ann. Chim. Analyt.*, 1923, **5**, 9; *J.*, 1923, 181A.

¹⁰⁸ *J. Assoc. Off. Agric. Chem.*, 1923, **6**, 407; *J.*, 1923, 791A.

¹⁰⁹ *J. Min. Agr.*, 1923, **29**, 944, 1044; **30**, 758, 870. See also *Min. Agr. Leaflet No. 398.*

process, in which the refuse, after preliminary sorting, is subjected to a fermentation in a closed chamber. This results in quite a useful organic manure.¹¹⁰

"Artificial farmyard manure," or "straw manure," made by the "Adco" process of Hutchinson and Richards,¹¹¹ has been tested in a number of field experiments in Kent and Essex,¹¹² in comparison with cow or bullock manure, with very encouraging results.

Calcareous and Magnesian Materials.

The value of magnesian limestone for soil treatment is a matter on which there is some difference of opinion, but the balance of the evidence is against the existence of any harmful effect of such treatment. This is supported by the results of J. G. Lipman, A. W. Blair, H. C. McLean, and A. L. Prince,¹¹³ who could find little difference in the effect of magnesian or ordinary limestone on crop yield or composition of the soil. Similar results were obtained by W. H. MacIntyre and J. B. Young,¹¹⁴ who found, however, that precipitated magnesium carbonate had a transient toxic effect; this they explained as due to the production in the first instance of relatively soluble magnesium silicate compounds, which are subsequently converted to less soluble substances. F. W. Morse¹¹⁵ has studied the effect of various fertilisers, when used in conjunction with calcium carbonate, on the hydrogen ion concentration of the soil solution. The effect of gypsum on Iowa soils has been found by L. W. Erdman¹¹⁶ to consist mainly in an increase in the soluble potash and phosphate. In the field a favourable effect on lucerne was obtained.

Under certain circumstances magnesium compounds appear to be of value as manures. Instances of this are found in the Rothamsted experiments on potatoes.¹¹⁷ O. Marholt has made a careful study of the influence of conditions on the action of magnesium salts on the yield of potatoes, and finds that it is evident only in the presence of organic manures such as dung.¹¹⁸ This interesting observation may serve to clear up some of the irregularities observed in the past.¹¹⁹

¹¹⁰ J. Bordas, *Ann. Sci. Agron.*, 1923, **40**, 77.

¹¹¹ See *Ann. Repts.*, 1922, **7**, 374.

¹¹² *Rothamsted Expt. Sta. Report*, 1921-22, p. 19. G. H. Garrad, *Agric. Gaz.*, 1923, **88**, 791.

¹¹³ *Soil Sci.*, 1923, **15**, 307; *J.*, 1923, 791A.

¹¹⁴ *Ibid.*, 1923, **15**, 427; *J.*, 1923, 1036A.

¹¹⁵ *Ibid.*, 1923, **15**, 75.

¹¹⁶ *Ibid.*, 1923, **15**, 137; *J.*, 1923, 617A.

¹¹⁷ *Rothamsted Expt. Sta. Report*, 1921-22, p. 19.

¹¹⁸ *Landw. Vers.-Stat.*, 1923, **100**, 315.

¹¹⁹ M. Popp and J. Contzen, *Landw. Jahrb.*, 1923, **58**, 313. E. A. Miescherlich and H. Wagner, *ibid.*, 1923, **58**, 645.

The value of magnesian manures for the counteraction of a chlorotic disease of tobacco has been demonstrated in the United States.¹²⁰

Sulphur Treatment.

To the outline of the subject given in last year's Report,¹²¹ and the general accounts given by J. G. Lipman,¹²² and by J. S. Joffe,¹²³ several points of detail may be added, although there has been no important change in the general position. Suitable conditions for the composting of raw phosphate with sulphur are being worked out by J. S. Joffe.¹²⁴ W. Rudolfs¹²⁵ has shown that by composting greensand with sulphur, water-soluble potash is produced, the resulting compost being suitable for the supply of potash to soy bean cultures. The relation of the moisture content of the soil to the effectiveness of sulphur oxidation in inhibiting the development of potato scab has been studied by W. H. Martin,¹²⁶ while J. S. Joffe and H. C. McLean,¹²⁷ and S. A. Waksman, C. H. Wark, J. S. Joffe, and R. L. Starkey¹²⁸ have further developed the use of sulphur oxidation as a means of improving "black alkali" soils. E. B. Reynolds and A. H. Leidigh¹²⁹ observed a favourable effect of dressings of sulphur, especially in presence of lime, on yields of cotton. This would appear to be an instance of the direct fertilising value of sulphur compounds in some soils, the possibility of which has been pointed out by C. O. Swanson and W. L. Latshaw.¹³⁰

Carbon Dioxide as a Fertiliser.

The influence of such factors as light intensity and moisture on the possibility of bringing about substantial crop increases by artificial enrichment of the atmosphere with carbon dioxide¹³¹ has been emphasised and investigated by A. Densch,¹³² A. Densch and C. Hunnius,¹³³ and by H. Janert.¹³⁴ From a consideration of the results of the latter, E. A. Mitscherlich has developed an inte-

¹²⁰ W. W. Garner, J. E. McMurtrey, C. W. Bacon, and E. G. Moss, *J. Agric. Res.*, 1923, **23**, 27.

¹²¹ See *Ann. Repts.*, 1922, **7**, 375.

¹²² *Ind. Eng. Chem.*, 1923, **15**, 404; *J.*, 1923, 565A.

¹²³ *New Jersey Agr. Exp. Sta. Bull.* 374, 1922.

¹²⁴ *Soil Sci.*, 1922, **14**, 479; 1923, **15**, 93; *J.*, 1923, 321A.

¹²⁵ *Ibid.*, 1922, **14**, 307.

¹²⁶ *Ibid.*, 1923, **16**, 69; *J.*, 1923, 1036A.

¹²⁷ *Science*, 1923, **57**, 53.

¹²⁸ *J. Agric. Res.*, 1923, **24**, 297; *J.*, 1923, 900A.

¹²⁹ *Soil Sci.*, 1922, **14**, 435; *J.*, 1923, 321A.

¹³⁰ *Ibid.*, 1922, **14**, 421; *J.*, 1923, 320A.

¹³¹ See *Ann. Repts.*, 1921, **6**, 413.

¹³² *Z. Pflanz. Düng.*, 1922, **1**, 32.

¹³³ *Ibid.*, 1923, **2**, B, 241.

¹³⁴ *Ibid.*, 1923, **1**, A, 177.

resting application of his mathematical treatment of the "Law of minimum" to the action of the two correlated growth factors of intensity of illumination and carbon dioxide content of the atmosphere.¹³⁵ He shows that under ordinary illumination in daylight out of doors the crop obtained without artificial enrichment of air was already 95.4% of the maximum obtainable under these conditions by using extra carbon dioxide. Under conditions of diminished illumination, however, such as obtain in greenhouses, where the lighting is, e.g., one-half or one-quarter of normal daylight, the yield obtained with the ordinary carbon dioxide content of the atmosphere was only 66.9% or 24% respectively of that obtainable by the use of increased carbon dioxide; in other words, the efficiency ("Wirkungswert") of carbon dioxide is much greater under greenhouse conditions than in the open in normal daylight. For the case of a greenhouse with an illumination of only 25% of normal daylight, he draws up the following table:—

| CO_2 in air, % | .. | 0.03 | 0.05 | 0.075 | 0.10 | 0.15 | 0.20 | 0.30 |
|---------------------------------|----|------|------|-------|------|------|------|------|
| Yields as % of maximum possible | .. | 24.0 | 57.6 | 66.3 | 76.6 | 88.8 | 94.5 | 98.7 |

The results of Bornemann and others, who claim that the crop increases they obtained in the open air were due to the increased carbon dioxide content of the air around the leaves, are regarded by Mitscherlich as due to the effect of other factors, such as the influence of the mulch on the soil moisture, and to the fact that their experimental conditions involved shading of the crop.

The assimilation of carbon dioxide by carrots and radishes in closed cylinders, and the effect of the manurial treatment and of meteorological conditions on the carbon dioxide content of the air around the growing crop in the field, have also been studied by H. Lundergårdh.¹³⁶

It would thus appear that it is for greenhouse work that the enrichment of the air with carbon dioxide is most likely to have a future. As a preliminary to a critical investigation of this side of the problem, O. Owen has studied the distribution of carbon dioxide in glasshouse atmospheres,¹³⁷ and the production of an atmosphere rich in carbon dioxide in a glasshouse.¹³⁸

SOILS.

In this section of the report attention is confined mainly to work on methods for the examination of the soil, leaving questions of a more theoretical nature for consideration in the Report to the Chemical Society.

¹³⁵ *Z. Pflanz. Jüng.*, 1923, 1, A, 211.

¹³⁶ *Angew. Bot.*, 1922, 4, 120; *J.*, 1923, 153A.

¹³⁷ *Ann. Appl. Biol.*, 1923, 10.

¹³⁸ O. Owen and P. H. Williams, *ibid.*, 1923, 11.

A survey of the vegetation and soils of Africa, including a general discussion of the classification of soils and the influence of climatic factors on their origin and nature, has been published by I. L. Shantz and C. F. Marbut.¹³⁹ A survey of British fruit soils is being undertaken.¹⁴⁰

Mechanical Analysis and Physical Properties.

The same principle as that used by G. W. Robinson for the mechanical analysis of the soil¹⁴¹ has been independently applied to the same purpose in the United States by D. S. Jennings, M. D. Thomas, and W. Gardner,¹⁴² and in Germany by G. Krauss.¹⁴³ The latter author has also described a simple graphical method for calculating the specific surface of the soil from the mechanical analysis. F. Zunker¹⁴⁴ defines the specific surface of a soil as the ratio of the total surface of the particles in a given weight of soil to that of an equal weight of a soil of which all the particles have a diameter of 1 mm. The wide variations in the values thus obtained, according to the type of soil, are shown by the following table:—

| Type of soil. | Specific surface (Zunker ¹⁴⁴) | | | |
|---------------|---|----|----|--------------|
| Heavy clay | .. | .. | .. | over 1000 |
| Ordinary clay | .. | .. | .. | 1000-730 |
| Heavy loam | .. | .. | .. | 730-510 |
| Ordinary loam | .. | .. | .. | 510-340 |
| Sandy loam | .. | .. | .. | 340-130 |
| Loamy sand | .. | .. | .. | 130-30 |
| Sand | .. | .. | .. | less than 30 |

Zunker specially emphasised the value of the determination of specific surface as a guide to the proper depth of drainage of a soil.

A source of error which is inherent in sedimentation methods of mechanical analysis, such as those of Odén,¹⁴⁵ Robinson, Jennings, Thomas, and Gardner, and Krauss, and indeed in all sedimentation methods not involving the repeated working up of the sediment until no matter remains in suspension after the specified time of settling (as in the standard British "beaker" method), arises from the fact that it is a matter of the greatest difficulty to bring about complete disintegration of compound particles and complete dispersion of a soil into a suspension of its ultimate particles. This difficulty is emphasised by the results of W. H. Fry,¹⁴⁶ who found, on microscopical examination of the sediments separated by

¹³⁹ "The Vegetation and Soils of Africa," (Amer. Geogr. Soc., N.Y., 1923).

¹⁴⁰ *J. Min. Agr.*, 1923, **28**, 867.

¹⁴¹ See *Ann. Repts.*, 1922, **7**, 379.

¹⁴² *Soil Sci.*, 1922, **14**, 485; *J.*, 1923, **320A**.

¹⁴³ *Int. Mitt. Bodenkunde*, 1923, **13**, 147.

¹⁴⁴ *Landw. Jahrb.*, 1923, **58**, 159.

¹⁴⁵ S. Odén, *Int. Mitt. Bodenkunde*, 1915, **5**, 251.

¹⁴⁶ *J. Agric. Res.*, 1923, **24**, 879; *J.*, 1923, **1085A**.

ordinary mechanical analysis, between 30 and 60% of the total soil colloids undispersed among the mineral particles.¹⁴⁷

R. V. Allison¹⁴⁸ has described a method, based on that used in ceramics, for measuring the tensile strength of dried blocks of soil, expressed as a modulus of rupture, which has given promising results in the study of alkali soils, and which shows up clearly the effect of lime in improving the physical condition of clay soils. The older method of Apterberg¹⁴⁹ has been studied by B. Tacke and T. Arnd,¹⁵⁰ and found to be incapable of showing up significant differences in the mechanical composition and physical condition of related soils. T. Arnd has developed a new method for measuring the coherence of mineral soils, based on the loss in weight sustained by a prepared cylinder and prism each consisting of a dried mixture of the soil with a small percentage of glass powder, when the prism and cylinder are ground down by pressure of the former against the latter, which is rotated under specified conditions.¹⁵¹

A. F. Joseph and F. J. Martin have investigated the effect of the soil : water ratio and of electrolytes such as calcium sulphate, ammonium sulphate, and sodium carbonate on the "moisture equivalent" of a number of Sudan soils, using the Briggs and McLane apparatus.¹⁵² The results show an apparent relation between the moisture equivalent and the clay content of the soils. F. Hardy¹⁵³ has made a further study of the "soil-point" method for directly estimating the water-supplying power of a soil in the field.

The use of mechanical pressure combined with suction for extracting the "soil solution" from the soil has been described by N. M. Tulaikov and M. S. Kusmin.¹⁵⁴ It is claimed that by this means considerable amounts of extract of constant composition may be obtained in 15 minutes, even from soils of low moisture content.¹⁵⁵

Soil Reaction.

Methods for the determination of soil acidity continue to provoke a considerable amount of research. R. M. Salter and

¹⁴⁷ R. O. E. Davis, *J. Amer. Soc. Agron.*, 1922, **14**, 293.

¹⁴⁸ *Ibid.*, 1923, **15**, 409.

¹⁴⁹ *Int. Mitt. Bodenkunde*, 1912, **2**, 149.

¹⁵⁰ *Ibid.*, 1923, **13**, 6.

¹⁵¹ *Z. Pflanz. Düng.*, 1923, **A 1**, 130.

¹⁵² *J. Agric. Sci.*, 1923, **13**, 49; L. J. Briggs and J. M. McLane, U.S. Dept. Agr. Bureau of Soils Bull. No. 45, 1907. See also G. J. Bouyoucos, *Soil Sci.*, 1922, **14**, 431; *J.*, 1923, 320A.

¹⁵³ *J. Agric. Sci.*, 1923, **13**, 355.

¹⁵⁴ *Soil Sci.*, 1923, **15**, 235; *J.*, 1923, 790A.

¹⁵⁵ For references to earlier pressure methods of obtaining the "soil solution" see P. S. Burgess, *Soil Sci.*, 1922, **14**, 191, and A. W. Groh, *Int. Mitt. Bodenkunde*, 1923, **13**, 107.

M. F. Morgan¹⁵⁶ find that the hydrogen-ion concentration of soil suspensions, determined electrometrically and also by sugar inversion, varies with the soil-water ratio, and they urge the need for specifying this value when stating the results of p_{H} measurements on soils. C. O. Rost and A. E. Fieger¹⁵⁷ find that usually, though not always, the hydrogen-ion concentration of the soil is increased somewhat by air-drying, and even more by oven-drying. The colorimetric method of measurement of hydrogen-ion concentration of the soil is frequently unsuitable owing to the turbidity of the soil extract.¹⁵⁸ C. T. Gimingham¹⁵⁹ recommends the use of a displacement method of obtaining the soil extract in order to get over the difficulty, but it is found that the values obtained are not always comparable with the true value as determined electrometrically. F. W. Parker and O. C. Bryan¹⁶⁰ find a fair correlation between the hydrogen-ion concentration and the results of the Truog test and the sugar inversion method. The inversion of sucrose is shown to be catalysed by the acid silicates of the soil, whereas the hydrolysis of ethyl acetate in soil suspensions is not so catalysed. F. W. Parker and J. W. Tidmore¹⁶¹ describe a modified form of the Truog test, in which the hydrogen sulphide is determined volumetrically.

The "lime requirement" of the soil does not bear a precise relation to the hydrogen-ion concentration,¹⁶² and the value obtained depends greatly on the method used. There is, however, usually a general correlation, especially on soils of a similar type. Such a correlation is observed by E. A. Carleton,¹⁶³ using the Jones calcium acetate method for determining lime requirement. Québec soils showed a positive value by this method up to p_{H} 7.6, but lime-water added to the soil in an amount corresponding to the indicated lime requirement brought about approximate neutrality. The same author¹⁶⁴ has studied the litmus paper method of testing the soil reaction. P. E. Karraker¹⁶⁵ has also established a correlation between the p_{H} of the soil, its lime requirement as determined by the Veitch and by the Hopkins methods, and the growth of clover. The fact that *Azotobacter chroococcum* will not grow in media with a p_{H} lower than about 6.0 was utilised by H. R.

¹⁵⁶ *J. Phys. Chem.*, 1923, **27**, 117; *J.*, 1923, 368A.

¹⁵⁷ *Soil Sci.*, 1923, **16**, 121; *J.*, 1923, 1142A.

¹⁵⁸ See e.g., A. F. Joseph and F. J. Martin, *J. Agri. Sci.*, 1923, **13**, 321; *J.*, 1923, 845A.

¹⁵⁹ *J. Agri. Sci.*, 1923, **13**, 69; *J.*, 1923, 466A.

¹⁶⁰ *Soil Sci.*, 1923, **15**, 99; *J.*, 1923, 617A.

¹⁶¹ *Ibid.*, 1923, **16**, 75; *J.*, 1923, 1035A.

¹⁶² See e.g., T. Wherry, *J. Wash. Acad. Sci.*, 1923, **13**, 97; *J.*, 1923, 512A.

¹⁶³ *Soil Sci.*, 1923, **16**, 79; *J.*, 1923, 1036A.

¹⁶⁴ *Ibid.*, 1923, **16**, 91; *J.*, 1923, 1142A. See also ¹⁷⁰.

¹⁶⁵ *Ibid.*, 1923, **15**, 473; *J.*, 1923, 1035A.

Christensen¹⁶⁶ in 1906 as the basis of a method for measuring the lime requirement of the soil, and this method has been widely applied in Denmark. Christensen has now studied a large number of Danish soils by this method and also by Hasenbäumer's¹⁶⁷ modification of Daikuhara's method, and by Comber's¹⁶⁸ method. He finds the last-named method to be much superior to many of the earlier methods for studying the soil reaction, but considers that the *Azotobacter* method still has a useful place and that none of the chemical methods is capable of entirely replacing it.¹⁶⁹ Comber's method has also been developed by D. J. Hissink¹⁷⁰ so as to render it applicable to alkaline soils as well as acid ones. In its modified form it is widely used in Holland, where it has proved to be of great value in the diagnosis of acidity as a cause of infertility in various soils.

The association of soil sourness with the presence of soluble aluminium in the soil is now well known. P. S. Burgess¹⁷¹ has described a method for the determination of this so-called "active" aluminium in the soil, depending on the extraction of the soil with $N/2$ acetic acid. His results show a correlation between the content of "active" aluminium and the lime requirement.

Mineralogical Analysis.

In the past little attention has been paid to the examination of soils by mineralogical methods, largely no doubt owing to the highly specialised nature of the knowledge and technique required. J. Hendrick and G. Newlands¹⁷² have described a relatively simple method for the mineralogical examination of the soil, in which the main fractions into which the soil is divided by mechanical analysis are each subdivided by means of flotation, using pure bromoform (sp. gr 2.9), combined with magnetic separation, into three groups:—(1) the orthoclase group, characterised by potash felspar; (2) the quartz group, characterised by quartz; (3) the ferrosilicate group characterised by ferromagnesian silicates and iron oxides. Each group is then examined microscopically. By this means the authors have made an interesting comparison of several English and Scottish soils.

Chemical Analysis.

The Estimation of "Available Plant Food" in the Soil.—Despite the enormous amount of work that has been done on this

- ¹⁶⁶ *Zentr. Bakt.*, 1906, **II**, **17**, 735; see also *Soil Sci.*, 1917, **4**, 115.
- ¹⁶⁷ J. Hasenbäumer and J. König, *Landw. Jahrb.*, 1921, **55**, 233.
- ¹⁶⁸ N. M. Comber, *J. Agric. Sci.*, 1920, **10**, 420.
- ¹⁶⁹ H. R. Christensen, *Int. Mitt. Bodenkunde*, 1923, **18**, 116. See also *Soil Sci.*, 1923, **15**, 329; *J.* 1923, 346A.
- ¹⁷⁰ Ref. in *Z. Pflanz. Düng.*, 1923, **2**, **B**, 491.
- ¹⁷¹ *Soil Sci.*, 1923, **15**, 131; *J.*, 1923, 617A.
- ¹⁷² *J. Agric. Sci.*, 1923, **18**, 1; *J.*, 1923, 465A.

subject, the soil chemist is unable to state with any degree of certainty, merely on the basis of a chemical examination, the manurial needs of any given soil.¹⁷³ He is nevertheless frequently expected to do so, it being a common experience for him to receive a sample of soil from a farmer with the request that he will analyse it and state in what respect it is deficient in plant food and what fertilisers are needed. In practice there is usually no difficulty in diagnosing a deficiency of lime, with which deficiency probably more cases of crop failure can be associated than with any other. With regard to nitrogen, the response to nitrogenous manures on most British agricultural soils is so definite that the benefit of such dressings at their proper places in the rotation is seldom called into question. The position is far otherwise as regards phosphorus and potassium. Practically any of the known methods will show up a soil in which the supply of either of these elements is at its lowest ebb; the difficult problem arises with soils which appear to contain at least a moderate amount of readily soluble phosphate and potash. Some such soils behave reasonably and respond to phosphatic or potassic manuring more or less as would be expected from their analysis, but soils are not infrequently met with which, on analysis, appear to contain a sufficiency, and on occasion even more than a sufficiency, of one or both of the elements in question, and which nevertheless prove in practice to be extraordinarily responsive to manuring with the fertilisers that would have been deemed unnecessary from the analytical figures. The result is that any agricultural chemist who values his reputation hesitates to give advice regarding the manuring of a soil unless he has available also the results of vegetation experiments, preferably on the field scale, on that or similar soils.

Without doubt, many cases of the failure of soil analysis to forecast the responsiveness of a soil to manuring may be explained by the operation of other limiting factors, the existence of which has been unsuspected or overlooked. The realisation of the complexity of the soil and of the factors which control crop production, and the increasing degree to which the mode of operation of these factors is being elucidated, enable the well-informed agricultural chemist to form an opinion as to the needs of a given soil with greater certainty than formerly. Although it is, in the nature of things, vain to expect that any solvent or method can be found which will give in all cases a clear and direct indication of the manurial needs of the soil, it is desirable to consider the relative merits of the many methods that have been proposed for this purpose.

The oldest and best known method for the estimation of the "available" phosphate and potash in the soil is that of Dyer,¹⁷⁴

¹⁷³ See e.g., Menozzi, *Chem. and Ind.*, 1923, 1083.

¹⁷⁴ B. Dyer, *J. Chem. Soc.*, 1894, 65, 115.

in which the soil is extracted with 1% citric acid. This method is the one commonly used in this country. In the United States preference is given to the use of $N/5$ hydrochloric or nitric acid.¹⁷⁵ On the Continent a considerable amount of work has been done on the subject by E. A. Mitscherlich, by J. König and J. Hasenbäumer, and by O. Lemmermann. Mitscherlich's method depends on the use of water-saturated with carbon dioxide.¹⁷⁶ König and Hasenbäumer, after studying a variety of methods, such as treatment with hydrogen peroxide, electrolysis, and heating in an autoclave at 5 atm. pressure, finally come to the conclusion that the Dyer method is generally the most suitable.¹⁷⁷ Lemmermann comes to the same conclusion as regards the estimation of "available" phosphate, but for the potash he prefers treatment with 10% hydrochloric acid.¹⁷⁸ C. Brioux¹⁷⁹ has found that for the special case of calcareous soils the Dyer method, owing to the neutralisation of the citric acid by the chalk, is not so suitable as the method of Schloesing and de Sigmund, in which the soil is treated with dilute nitric acid of such strength that its final concentration is between 0·02 and 0·1%.

In general, the balance of evidence is in favour of Dyer's method for phosphates. Lemmermann regards the ratio of citric-soluble to total phosphates in the soil, which he terms the "relative solubility," as the important value, inasmuch as it takes account of the fact that in different soils the phosphate may exist in forms with widely differing solubility.¹⁸⁰ Bearing in mind, however, that this ratio, even if high, does not indicate a sufficient supply of phosphate if the total amount in the soil is low, it is not clear that Lemmermann's value possesses any great advantage over the value for citric-soluble phosphate alone.

For potash the position is more doubtful; it is possible that the method recently worked out by Hissink¹⁸¹ may prove of value in estimating the availability of this nutrient in the soil.

As an alternative to the analysis of the soil, that of the plant grown on the soil in question has been suggested as an obvious

¹⁷⁵ O. M. Shedd, *Soil Sci.*, 1923, **15**, 383; *J.*, 1923, 846A. G. S. Fraps, *J. Assoc. Off. Agric. Chem.*, 1923, **8**, 329; *J.*, 1923, 414A.

¹⁷⁶ E. A. Mitscherlich, "Bodenkunde" (Berlin, Parey), 1920, p. 201.

¹⁷⁷ J. König and J. Hasenbäumer, *Landw. Jahrb.*, 1923, **59**, 97; J. König, J. Hasenbäumer, and J. Schafers, *ibid.*, 1923, **58**, 55; J. König, J. Hasenbäumer, and E. Kroger, *ibid.*, 1923, **58**, 87; J. König, J. Hasenbäumer, and K. Kuppe, *ibid.*, 1923, **59**, 65.

¹⁷⁸ O. Lemmermann and L. Fresenius, *Z. Pflanz. Düng.*, 1923, **2 A**, 363. See also O. Lemmermann, L. Fresenius, and H. Wiessmann, *Landw. Vere.-Stat.*, 1921, **98**, 155.

¹⁷⁹ Ann. Sci. Agron., 1922, **39**, 82.

¹⁸⁰ See also Engels, *Z. Pflanz. Düng.*, 1923, **2 B**, 185.

¹⁸¹ See *Ann. Repts.*, 1921, **6**, 415; also *Soil Sci.*, 1923, **15**, 269; *J.*, 1923, 791A.

means of estimating how much of the nutrient material in the soil is available for plant growth.¹⁸² The difficulty of using full-grown plants for this method consists largely in the need of first ascertaining the composition of an average plant of the sort used in the experiment. Much of König and Hasenbäumer's work¹⁷⁷ was concerned with this point. In a recent paper by H. Neubauer and W. Schneider¹⁸³ an attempt is made to get over this difficulty by growing a large number of seedling plants (rye) in a small amount of the soil under investigation, so that the whole of the soil is completely penetrated by the roots. It is concluded that after the lapse of 18 days the whole of the readily available phosphates and potash in the soil will have been absorbed; the plants are then separated from the soil and analysed. This method gave quite promising results and it merits further trial.

An interesting application of the use of the plant as a means of estimating the manurial needs of the soil is that developed by H. Walker¹⁸⁴ for the soil of sugar plantations. The phosphate and potash in the sugar cane juices were determined, and it was found that a content of less than 0·02% and 0·05% of P₂O₅ and K₂O respectively in the juice was an indication of the need for phosphate or potash manuring.

The ultimate criterion of the need of a given soil for manuring must always consist of vegetation experiments in pots and in the field, in which is determined the actual effect on crop yield of a given fertiliser under conditions excluding the action of non-manurial limiting factors (pot experiments), and under natural conditions (field experiments).¹⁸⁵ A critical experimental comparison of all the more promising of the chemical methods on a series of widely representative soils on which field and pot experiments are also carried out, is much to be desired.

General.—From a study of the variability of certain soils in total and nitrate nitrogen, A. L. Prince¹⁸⁶ shows that many more samples must be taken for the determination of the latter than for that of the former. C. T. Gimingham and R. H. Carter¹⁸⁷ have demonstrated a source of error in the determination of nitrates in soils by the phenoldisulphonic acid method, arising from the

¹⁸² See e.g., A. D. Hall, *J. Agric. Sci.*, 1905, **1**, 65.

¹⁸³ *Z. Pflanz. Düng.*, 1923, **2 A**, 229.

¹⁸⁴ H. Walker, *Ind. Eng. Chem.*, 1923, **15**, 164; *J.*, 1923, 322A. H. Walker and G. B. Glick, *Int. Sugar J.*, 1923, **25**, 478; *J.*, 1923, 1086A.

¹⁸⁵ For an interesting discussion of the application of Mitscherlich's well known mathematical treatment of the relation between crop yield and growth factors, to pot cultures and field experiments, as a means of ascertaining the manurial requirements of the soil, see E. A. Mitscherlich, *Landw. Jahrb.*, 1923, **58**, 125, 601.

¹⁸⁶ *Soil Sci.*, 1923, **15**, 395; *J.*, 1923, 846A.

¹⁸⁷ *J. Agric. Sci.*, 1923, **13**, 60; *J.*, 1923, 466A.

fact that certain kinds of filter paper retain nitrate. W. M. Gibbs, R. E. Neidig, and H. W. Batchelor¹⁸⁸ have described an aeration method for the determination of ammonia in alkali soils.

L. J. Simon¹⁸⁹ has found that the use of silver dichromate in place of chromic acid in the sulphochromic method for the determination of carbon in soils gives higher and more accurate results. This has been confirmed by V. Agafonoff.¹⁹⁰ K. A. Bondoroff and H. R. Christensen have described a volumetric permanganate method for the determination of organic matter in decomposition experiments with soil.¹⁹¹

Biological Examination.

Basing his technique on the difficulty of effecting a complete dispersion of the colloidal matter in a soil suspension by ordinary means (see p. 424), C. L. Whittles¹⁹² has developed a new method for ascertaining the numbers of bacteria in the soil. This method gave enormously higher numbers than that usually obtained, but H. G. Thornton¹⁹³ has shown that the results obtained by Whittles' method are impossibly high, and has suggested that they are brought about by incomplete sterilisation of the special apparatus used for obtaining the soil suspension. S. A. Waksman¹⁹⁴ has discussed the various factors which influence the nitrifying power of the soil and has outlined a scheme for the determination of this property.

¹⁸⁸ *Soil Sci.*, 1923, **15**, 261; *J.*, 1923, 791A.

¹⁸⁹ *Comptes rend.*, 1923, **176**, 1409; *J.*, 1923, 670A.

¹⁹⁰ *Ibid.*, 1923, **177**, 404; *J.*, 1923, 941A.

¹⁹¹ *Soil Sci.*, 1923, **15**, 361; *J.*, 1923, 846A.

¹⁹² *J. Agric. Sci.*, 1923, **13**, 18; *J.*, 1923, 466A.

¹⁹³ *Ibid.*, 1923, **13**, 352; *J.*, 1923, 846A.

¹⁹⁴ *Soil Sci.*, 1923, **15**, 241; *J.*, 1923, 790A.

SUGARS, STARCHES, AND GUMS.

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SUGARS.

Statistical.—The developments of the year accorded closely with the views expressed in last year's report. Early in February the reduction in the first estimates of the Cuban crop from 4,192,000 tons to 3,800,000 (actually 3,602,910) was followed by an immediate rise in price, which continued during the first half of the year, when the price of Cuban sugar rose to £33-34 per ton c.i.f. A decrease in the consumption in the United States for the first six months of the year of 2·56%, as compared with the similar period of 1922, and, also, a reduction of 52,294 tons in this country for the same six months as compared with 1922, together with increased deliveries of sugar from other sugar-producing countries, like Java, Peru, Mauritius, and Brazil, had eventually a depressing influence on prices. For the calendar year the consumption of sugar in the United States and United Kingdom shows a decline of about half a million tons, as compared with 1922. For the sugar year 1922-3, the world's consumption is estimated at about 19,250,000 tons against a production of 18 million tons. Clearly, therefore, the carry-over of 1,203,000 tons from the previous year will be fully exhausted, and invisible supplies be at an exceedingly low level at its close. Such a statistical position has naturally caused a general rise in price, but this has been checked, partly by adverse trade conditions and partly by the influence exerted by the forthcoming European beet sugar crop, which may be about 200,000 tons larger than its immediate predecessor. The world's new crops are estimated to produce an increase of a million tons over last year, but are likely to be no more than will meet requirements. With a constantly growing world consumption, which has practically doubled in the last thirty years, the origin of sugars for the British market is a matter of considerable significance. The fact that Cuba produces 22% of the total world production is of serious consequence to us in seasons of partial failure there; while, at the same time, it has to be realised that our own colonies, enjoying a preference of one sixth of the full duty, have supplied the United Kingdom, during the first nine months of the year, with only 18% of its total importations. The desirability of increasing supplies

from Empire sources is recognised, not only from the colonial viewpoint, but, generally, as a means of minimising the violent fluctuations in price due to the present dominating influence of the Cuban crop.

THE CANE SUGAR INDUSTRY.

Extraction of the juice.—In the majority of cases, the cane on receipt at the factory passes directly to the crushers and mill proper. These crushers, and the function they play in disintegrating the cane and bringing it into a suitable condition for the subsequent milling operations, have been fully described in former Reports.¹

A very ingenious machine recently devised by F. Maxwell² combines in itself a pair of pressure rollers, with pressure-regulating gear, and a third shredding roller working in conjunction with one of the pressure rollers. The crushing or pressure rollers are driven through reduction gearing from a shaft from which also the shredding roller is driven at high speed through belt gearing. As the cane is delivered down a chute it is first crushed by the rollers and immediately thereafter shredded by the high-speed roller. A trough placed in position below catches the juice, while a casing, placed in suitable position, prevents the shreds of cane from dispersing and delivers them to a conveyor. One of the crushing rollers may have a circumferentially grooved surface, and the other is provided with teeth or projections or grooves of any known form. The toothed shredding-roller may be formed of discs assembled together. The operation of this plant, on a practical scale, will be watched with extreme interest.

Coming now to the train of mills where the actual extraction of the juice takes place, it has been known for some years that when the mill-rollers are made with suitably arranged circumferential grooves, the juice runs away more freely from the pressed cane and consequently better extraction and increased capacity result. Considerable difficulty is experienced, however, in keeping the grooves free from bagasse, and scrapers for this purpose are commonly in use. The method of grooving mill-rollers devised by H. C. Hinton and C. A. Marsden³ has been found to minimise this drawback; and R. Harvey describes⁴ the improved results obtained at Funchal, Madeira, with this type of roller, in trials made this year, when a 2·9% increase in extraction was obtained, and the general mechanical running of the mill was greatly improved. Owing to the enormous grip exerted by this form of grooved roll, the mill rolls can be set tighter than before, while the usual rate of milling is maintained. For the conveyance of the cane from one

¹ *Ann. Repts.*, 1920, 5, 389-390; 1922, 7, 385-386.

² E.P. 198,120.

³ E.P. 189,216.

⁴ *Intern. Sugar J.*, 1923, 462.

set of mills to the next following, the Meinecke chute,⁵ with its absence of moving parts and general simplicity of construction, is reported⁶ to be giving excellent results in Hawaii and Louisiana.

With the enormous pressure to which the cane is subjected by modern mills, the exhausted or crushed cane, known as bagasse, generally leaves the mill with a water content which may vary from about 43% to 50%. A very remarkable reduction in this percentage is claimed to be obtainable by W. Geveke⁷ in his system of extraction of juice from the cane by shredding, macerating, and pressing. After crushing and shredding, the cane is sprayed with warm water or moist steam and led by means of carriers to plunger presses. There the material is subjected to a high pressure, 10,000 lb. per sq. inch, for about a minute, with the result that the juice is expressed, leaving a bagasse, containing 25% of water, ready for transmission to the boilers for steam raising purposes. This pressure is said to be double and the duration of the pressure about four times that obtainable in a modern milling plant, and the cost about half that of the ordinary recognised types of plant. Before expressing an opinion regarding the claims here made, there are many details one would like to know, e.g., the tonnage of cane (or fibre) treated per hour, the quantity of water used and the composition of the bagasse, particularly with reference to the amount of sugar left in it. It may, further, be permissible to point out that N. Deerr,⁸ in an exhaustive series of experiments in the extraction of juice by mills, found that fineness of division and repeated pressings are of more importance than a smaller number of pressings at largely increased pressures.

During the year improvements in the design of mill rollers have been made by H. W. Aitken,⁹ and in the method of regulating hydraulic apparatus for cane mills by D. Stewart and others.¹⁰

Clarification.—For long the need has been realised of an efficient strainer for the juice coming from the mills, and it is satisfactory to know that of recent efficient types of strainers, one invented by S. S. Peck,¹¹ of a revolving pattern, has stood the test of trial in Hawaii, with results, according to W. G. Hall, exceeding expectations.

The procedure adopted in "tempering" or defecating the juice varies in different localities, for various reasons. For example, in Louisiana,¹² at one of the larger factories, the method was tried of

⁵ *Ann. Repts.*, 1922, 7, 386.

⁶ *Facts about Sugar*, 1923, 17, 40.

⁷ E.P. 196,224; J., 1923, 568A.

⁸ "Cane Sugar" (1921 Edit.), p. 188.

⁹ E.P. 187,095.

¹⁰ E.P. 190,917.

¹¹ *Intern. Sugar J.*, 1923, 25, 432.

¹² *Ibid.*, 482.

adding milk of lime¹³ of 11° B. to the cold juice as it entered the juice strainer. While improved clarification resulted by this process, it was found that all the lime could not be added at that stage, owing to the formation of the organism *Leuconostoc*, which is sometimes called "frog spawn," in the tanks and pipes when the juice became alkaline, and the balance of the lime required was, therefore, added at the liming tanks. In Hawaii,¹⁴ various modifications in clarification practice have been tried, and certain conclusions drawn. For example, adding lime continuously at the mill has not been particularly successful in practice, on account of the alkaline juices dissolving insoluble impurities from the bagasse; but, on the other hand, defecation at the liming tanks carried to a degree of alkalinity higher than practised before, has been more generally adopted with satisfactory results.

Rather striking evidence of the advantages claimed to be gained by high additions of lime is to be found in a series of tests made by H. F. Hadfield¹⁵ in Hawaii. In order to avoid serious losses, not attributable to mechanical causes, but presumed to be due to inversion, liming of juice was resorted to to the extent of 25—70% in excess of that requisite to produce clarification with a neutral reaction, while the reaction at settling tanks and presses, and of sweet waters used for maceration, was always kept alkaline. As a result, the undetermined loss fell from 4·19% to 0·7–1·06%, while the boiling-house recovery was increased by 4–5%. No disadvantages incidental to this method of working were apparent, beyond the appearance of *Leuconostoc*, which was not in serious amount. It is stated that, notwithstanding the excess of lime used, it was impossible to drop an alkaline low-grade massecuite. Coupled with the fact that the gravity-purity of the final molasses increased, by this method of working, from 35·42 to 38·12, this would seem to indicate a destruction of reducing sugars with the formation of glucinic and saccharinic acids. As one would naturally expect, the clarified juices were very dark in colour. It is to be noted that such alkaline working as is here described, would probably result in the production of a raw sugar dark in colour, making the refiner's subsequent task correspondingly difficult.

When one turns, however, to consider special processes for the manufacture of plantation white sugars, the advantage of excessive liming with the immediate precipitation of the excess by carbon dioxide or sulphur dioxide gas is very apparent.

A very exhaustive and interesting comparative study of the relative advantages of carbonatation and sulphitation, as these processes are termed, has been made by F. Maxwell,¹⁶ with special

¹³ *Intern. Sugar J.*, 85, 204.

¹⁴ *Facts about Sugar*, 1922, 15, 480, 488; *J.*, 1923, 1191A.

¹⁵ *Intern. Sugar J.*, 1923, 25, 572.

reference to the manufacture of white sugars from that exceedingly gummy cane known as the Uba variety. The difficulties of working this cane in South Africa, owing to the "gums," are very great at all stages of operation. Owing to the relatively small quantity of lime used in sulpho-defecation factories, it is found that the gums are not wholly removed and in consequence the subsequent operations are only carried through with great difficulty; particularly is this the case at the filter presses and vacuum pans. In order, therefore, to deal with the gums in this notorious cane, much heavier liming is required, and the carbonatation process (which takes 7-10 times the amount of lime used in sulphitation) has been found to effect a more thorough clarification and to ensure the rapid and uninterrupted run of all the manipulations which are the essential requirements in the manufacture of white sugar. The figures quoted by Maxwell in comparing the two methods of clarification are extremely interesting. In the years 1917 and 1918, when sulphitation was employed, the figures for sucrose in the press cake were 8.57 and 9.69% respectively; while, for the three years of carbonatation practice, the figure was 5.99% for 1920, 2.35% for 1921, and 0.67% for 1922. The yields of white sugar are substantially increased by the carbonatation process, the difference in yield (as compared with sulphitation) being greater the more refractory and gummy the juices are.

As part of the question of the actual amount of lime that is to be added to cane juices, whether for defecation purposes alone, or in the white sugar processes where larger quantities are used, there has to be considered the mode of application. When, in common practice, milk of lime is run into the juice at strainers or liming tank, or, in special processes, at sulphiting or carbonating tanks, there is considerable risk of local over-liming, due to imperfect mixing. Products of decomposition of glucose and colour are formed, all prejudicial to good work. This difficulty has been referred to several times during the year, and D. J. W. Kreulen¹⁶ has put forward a method of reducing this trouble, which consists in distributing the milk of lime throughout the juice by means of air blown through an atomiser, and has also designed a special apparatus for carrying this idea into practice. Although it is held by some experts to be almost impossible to control the addition of lime by an automatic device with satisfactory results, owing to the constant variation in the nature of the juice to be treated, N. A. Helmer¹⁷ made trials, which he considered of some value, using a modified water-softener fitted with a special regulating arrangement, which allowed variable quantities of milk of lime to pass according as the juice required.

¹⁶ *Intern. Sugar J.*, 1923, **25**, 409.

¹⁷ *La. Planter*, 1922, **49**, 103.

A matter on which considerable difference of opinion may legitimately exist is the determination of the actual amount of lime needed for satisfactory defecation, and a complete knowledge of all the factors applicable to any particular case is necessary to form a right judgment. In the majority of factories the reaction of the juice with litmus and phenolphthalein papers is taken as a sufficient guide, the lime being added until any acidity as shown by litmus is neutralised or even until a slight pink coloration is shown on the phenolphthalein paper. While this may suffice, with proper attention, to produce the desired results, the subject has recently received consideration from H. F. Brewster and W. G. Raines, jun.,¹⁸ by J. Beobide,¹⁹ and by W. J. Williams and J. A. Gebelin²⁰ from the point of view of the hydrogen-ion concentration of the juice. Reference to this matter, and the work particularly of Brewster and Raines and of Beobide, is made later in the Report in the section dealing with Chemical Control, but the practical tests made by Williams and Gebelin of this method of controlling clarification over a whole season's campaign in Santo Domingo may with advantage be considered here. These investigators used the drop test on hot juice, and found the indicators suggested by Brewster gave quick and satisfactory tests. The p_h value necessary to obtain good clarification varied widely from 8.5 to 6 or less according to the juice. In the opinion of these chemists, it is evident that it is impossible to stipulate, and adhere to, a definite p_h value invariable for all juices. As indicative of improved clarification resulting from this method of control, the sugars turned out of this factory contained only 48.5 parts of insoluble matter per 100,000. In the course of working juice from cane grown on old fields, it was also found that no change of p_h could clarify it completely, and on investigation it was shown that this was due to silica in a colloidal form; further, it was surmised that a silicious deposit found on the evaporator tubes came from this haze in the juice. In this connexion, it may be recalled that Muller²¹ drew attention to the unsatisfactory defecation due to colloidal silica in organic combination, and suggested as a remedy the superheating of the raw juice to 116°C. This subject has already received considerable attention from M. Bird,²² and recently R. G. W. Farnell,²³ the Research Chemist of the British Empire Sugar Research Association, has published the result of some investigations on the effect of superheating unlimed cane juices. A laboratory experiment showed that 59.5% of the silica

¹⁸ *Intern. Sugar J.*, 1923, 25, 88.

¹⁹ *Sugar News*, 1923, 4, 65.

²⁰ *Facts about Sugar*, 1923, 17, 202.

²¹ *Ann. Repts.*, 1921, 8, 421.

²² *La. Planter*, 1922, 49, 81.

²³ *Intern. Sugar J.*, 1923, 358; *J.*, 1923, 991A.

in the juice is precipitated at 103° C. and 75.7% at 116° C. The important item, "glucose ratio," is not given in detail, but it is stated that it fluctuated considerably, showing increases and decreases from the raw juice figure. Factory tests were made at temperatures varying from 103.5° to 121° C., and, while the abulated comparisons are not of figures obtained during identical grinding periods, it is possible to conclude that part of the silica present is precipitated and that there is a decomposition of some of the gums resulting in a reduction of the lime required for satisfactory defecation.

Among the vital points remaining for further investigation is the connexion between the hydrogen-ion concentration of the raw juice and the inversion of sucrose during superheating. In view of experiments made by Deerr,²⁴ Brewster and Raines (*loc. cit.*), Leban,²⁵ and others, it may be that the possible loss of sucrose by inversion at "acidities," in terms of hydrogen-ion concentration, is under better control when this principle of ionic dissociation is employed as the guiding factor.

An apparatus for use in the high-temperature clarification of cane juices has recently been invented and patented by Duncan Stewart and Co., Ltd., and W. Mauss.²⁶ It is known that the gummy substances precipitable by heat and pressure are inclined to disintegrate, and in this condition are liable to choke quickly the surfaces of any filter used. In the Mauss system, the heated juice is passed through a series of tubes designed to prevent the coagulated albuminous matter from breaking up; in consequence, the filtration difficulties are, it is claimed, reduced.

Evaporation.—If the processes of defecation and filtration have been satisfactorily carried out, there results a clarified juice containing about 85% of water ready for concentration. This operation is carried out in two stages, firstly, by means of multiple effect evaporators and, secondly, in the vacuum pan, where the concentration is carried to the graining point. One source of trouble, common to both evaporating systems, is the risk of loss of sugar by entrainment in the vapour. In the first-named system, the loss takes place in the last effect, where the vacuum is highest and may be 26–27 inches. E. Haddon²⁷ found serious losses in the last vessel of a quadruple evaporator, but by installing a "save-all" of the type invented by N.A. Helmer,²⁸ which he slightly modified, he brought these losses down to a negligible amount. In Hawaii a number of factory managers have been experimenting with different

*²⁴ *Intern. Sugar J.*, 1916, 561.

²⁵ *Lg. Bull.*, 1920, No. 175.

²⁶ E.P. 194,948; *J.*, 1923, 468A.

²⁷ *Rev. Agric. de l'Ile Maurice*, 1922, 274; *J.*, 1923, 282-283A.

²⁸ E.P. 125,939; *Intern. Sugar J.*, 1920, 22, 288.

devices to lessen the loss by entrainment, and A. Fries²⁹ presented evidence showing that in several factories the well-known Stillman form of "save-all" was found only to reduce and not entirely to eliminate loss of sugar from this source, which result is contrary to the experience of most users of this trap. It was, however, found possible to reduce entrainment to a reasonable limit by the installation of wooden baffles for the purpose of reducing the velocity of the vapour passing through the apparatus. This device proved effective, even when running the factory at the rate of 40 tons of cane per hour, while at a lower rate of evaporation no sugar at all would be detected in the condensed water by means of the sensitive *a-naphthol* test. The concentration proceeds in the evaporator until generally a syrup containing about 50% of water is obtained. At this point the syrup is passed to the vacuum pan to be grained.

Boiling to Grain and Crystallising.—The boiling methods now most commonly adopted in raw sugar factories are directed largely towards obtaining only a marketable sugar of about 96° polarisation and an exhausted molasses of 35° purity or thereabouts. In order to obtain this result, as W. Searby³⁰ points out, it is inevitable that there should be a boiling-back of molasses and dark-coloured low-grade sugar, with the result that the marketable sugar is built up in an impure mother liquor containing too much non-sucrose, in every way detrimental to the colour and the yield. A study therefore has been made by H. C. Welle³¹ of the pan-boiling systems, in respect of the in-boiling of non-sugars. In great detail, he contrasts four systems and comes to the conclusion that the one which is preferable, both from the point of view of the plantation and the refinery, consists in boiling two raws and a low grade which is double-purged.

Simple as this statement may appear, the actual operation of producing a maximum yield of sugar, together with an exhausted molasses of low purity, is a difficult problem which has engaged the attention of technologists for many years. A recent Report³² drew attention to one of the factors affecting the purity of exhausted molasses, viz., the presence of fine grain, and, again, the whole subject has been reviewed by T. van der Linden³³ in an investigation on the nature of Java molasses. As a result of a study of the question by the Chemical Department of the Java Experiment Station, two conclusions were arrived at: firstly, that Java molasses should be regarded as a saturated solution of sucrose, the

²⁹ *Intern. Sugar J.*, 1923, 25, 591.

³⁰ *Ibid.*, 1923, 308.

³¹ *Ibid.*, 1923, 310.

³² *Ann. Repts.*, 1921, 6, 423.

³³ *Intern. Sugar J.*, 1923, 25, 531; *J.*, 1923, 1191A.

sucrose content of which is governed by the influence exerted on the solubility by the different constituents, viz., invert sugar and non-sugars; and, secondly, from the evidence obtained experimentally, that the further exhaustion of Java molasses is possible. These conclusions being accepted by van der Linden as scientifically sound, the question resolved itself into one of ascertaining in what manner, technically, they could be proved and carried into practice.

With the aid of a small experimental installation molasses were boiled to a high Brix degree (95° - 98.5°), at which gravity they were just movable in the crystalliser at the ordinary temperature. When this point was reached molasses at about 85° Brix was added in quantity sufficient to enable centrifuging to be effected. As a result of boiling to a high Brix, and centrifuging at as high a Brix as possible and at as low a temperature as possible (30° C.), a molasses was obtained having a purity 1.9° lower than one boiled by the customary method. In order to ensure the best conditions for obtaining an exhausted molasses by this method of boiling and centrifuging, the only part of the ordinary equipment of the factory that must be increased is the cooling capacity, so that the molasses may have three or four days in which to deposit its sucrose. H. C. Prinsen Geerligs,³⁴ whose classic investigations on this subject are well known, is in general agreement on the whole with van der Linden's experiments and results as indicating how the purity of exhausted molasses may be lowered and the sugar therein diminished, but is of opinion that they have not elicited anything previously unknown.

It may be recalled that Geerligs,³⁵ in a criticism of a process patented by J. N. S. Williams,³⁶ eight years ago, drew attention to methods outlined by him in his books, by which molasses is boiled in a vacuum pan on *pied-de-cuite* of crystals till a mixed massecuite of 60° purity and 98° Brix results. When this is cooled in motion for three days and centrifuged in ordinary Weston centrifugals, it is separated into an after-product sugar and a final molasses of about 30° purity. It has further to be observed that, however desirable it may be to centrifuge a heavy massecuite at as low a temperature as possible, the natural viscosity of molasses renders such an operation almost impossible, and therefore Geerligs had indicated a temperature of 45° C., below which it is inadvisable to go.

Deterioration of Raw Sugars.--The factors affecting deterioration of raw sugar in storage and transit have already received much attention and been adequately dealt with in recent Reports.³⁷ A solution of the problem has been announced by W. L. Owen,³⁸ who

³⁴ *Intern. Sugar J.*, 1923, **25**, 535.

³⁵ *Ibid.*, 1917, **19**, 159.

³⁶ E.P. 16,799 of 1915.

³⁷ *Ann. Reps.*, 1919, **4**, 385; 1921, **6**, 424.

³⁸ *Intern. Sugar J.*, 1923, **25**, 371; *J.*, 1923, 992A.

attacks it from the bacteriological side. It is well known that certain torulæ produce abnormal fermentative changes in sugar at the expense of the lævulose of the invert sugar present, with the usual evolution of carbon dioxide. Owen has found that by inoculating raw sugar with torulæ, the action of the moulds (which he has previously described as the most dangerous group of micro-organisms in sugar) was entirely restrained notwithstanding the fact that the fermentative changes brought about by the torulæ produced a lowering of the dryness of the molasses film, a condition which was most favourable to the invertive action of the moulds, *Aspergillus repens* and *A. niger*, which he employed. This restraining influence he attributes to the toxic effect of the carbon dioxide evolved upon the mould fungi. In the case of *Aspergillus repens*, the most active of the moulds occurring in deteriorating sugars, the concentration of carbon dioxide required to prevent growth at 15°-18° C. was found to be 40%. In the experiments made by Owen, under carefully controlled conditions, the effect of inoculation was most marked. In those cases where the film of fermenting molasses was present, no deterioration was observed, whereas in others, in which torulæ were absent, there was a loss of 6% of sucrose. These researches are still proceeding with the object of ascertaining the most suitable type of torulæ and the best methods to employ them on the industrial scale. Meanwhile the results obtained and the proposals made will be scrutinised closely by those whose work has not hitherto led them to similar conclusions.

It is generally agreed that the cause of deterioration of sugar in store or transit is due to the action of micro-organisms, but the problem is complicated by the chemical and physical nature of the sugars and by atmospheric and climatic conditions. Fully realising the correlation of causes, C. A. Browne³⁹ has been investigating the moisture absorptive power of different sugars under varying conditions of atmospheric humidity, and, independently, W. L. Owen⁴⁰ has been studying some of the factors affecting the moisture absorption of raw and refined cane sugars.

Browne's experiments elicit the interesting fact that lævulose ranks eleventh in order out of a range of seventeen substances, when subjected to a 60% humidity for one hour at a temperature of 20° C., but on exposure to a completely saturated atmosphere for 25 days, its position had changed to fourth in the list and its absorptive power was not exhausted.

As supplementary to these figures, Owen's⁴¹ study of the same subject reveals the fact that the moisture absorption of the samples of sugars (plantation whites and standard refined granulated) was

³⁹ *La. Planter*, 1923, 70, 7.

⁴⁰ *Ibid.*, 1923, 70, 88.

⁴¹ *Loc. cit.*

50% greater at 30° C. than it was at 23.5° C. Owen's contention that it is impossible to manufacture and store in perfectly aseptic conditions is well supported by others. Nevertheless, all emphasise the necessity of cleanliness in the factory as a preventive measure, and Owen quotes the satisfactory results obtained in Hawaii by strict attention to this important point.⁴² This year the same testimony comes from the Philippines. W. E. Kopke⁴³ reports the results of successful efforts made to reduce loss of sugar by inversion, by paying greater attention to juice strainers, the slats of the cushion-cushion conveyors, and the pipes leading to supply tanks, and A. W. Woods⁴⁴ finds a marked improvement in the reduction of slimy growths and sucrose-destroying ferments by the application of steam at different places where infection is liable to occur.

The caked condition of raw sugar as delivered at the refinery has been frequently observed and adversely commented upon, owing to the trouble of removing the sugar from the bag and the damage suffered by the bags in consequence. Causes of these objectionable features and suggestions for remedying them have been made by E. Wuthrich⁴⁴ and H. Walker.⁴⁵ The practice of bagging hot sugar in the factory and piling the bags, one on top of the other, until a very considerable weight rests on the lower tier, is believed by the former to be a contributory cause of caking, but not the main factor. From experiments made in factory and laboratory, Wuthrich concludes that caking follows when sugars, containing a fairly high moisture content, say, 1% or more, are brought into surroundings where they are partially or wholly dried. This is practically the opinion of Walker, who thinks, among other reasons which he specifies, that a humid atmosphere depositing moisture on the sugar, induces some sugar to pass into solution; while if, later, the atmosphere becomes dry, water evaporates from the film, causing supersaturation and crystallisation, the result being a cementing of the separate crystals. As both of these experts point out, among the chief means of preventing sugars from caking, it is necessary to dry and cool the sugar as much as possible before bagging and storing.

THE BEET SUGAR INDUSTRY.

Home-grown Sugar.—Evidences are not lacking of increasing interest in the cultivation in Britain of sugar beet and manufacture of sugar therefrom. Encouraged by the prospect of immunity from a high excise duty (amounting at present to about £25 per ton),

⁴² *Sugar News*, 1923, 4, 69.

⁴³ *Ibid.*, 1923, 4, 70.

⁴⁴ *Intern. Sugar J.*, 1923, 25, 192; *J.*, 1923, 670A.

⁴⁵ *Ibid.*, 1923, 25, 161; *J.*, 1923, 467A.

by the hope of financial and agricultural benefits accruing to the farmers, and by the monetary and technical assistance offered by The British Sugar Beet Growers' Society, Ltd., schemes have been formulated which are likely to materialise in the erection of new factories in Suffolk, Yorkshire, and South Lincolnshire in the near future, while agriculturists in other English Counties seem favourably disposed towards the erection of a central beet sugar factory. The two existing beet factories, Kelham and Cantley, will be merged into one company in the spring of 1924. Meanwhile the nominal capital of the former has been drastically reduced by writing off 15s. in the £. The English Beet Sugar Corporation (working Cantley) concluded their last season's operations with a net profit of £103,981, which enabled them to reduce their debit balance of £118,940, leaving £14,958 as a debit on profit and loss account to be wiped out, probably, in the current year. Some interest and other charges, amounting to £20,952, have also still to be liquidated. These factories co-operated in the campaign of 1922-23, to the extent that the roots of both areas, amounting to 54,000 tons, were all worked at Cantley, Kelham remaining idle. The working results are considered satisfactory. The average sucrose content of the roots was between 16 and 16½% and the extraction, in terms of white sugar, reached, for the first time in England, 13%. The price paid to the farmers for roots was 32s. f.o.r., based on a 15½% sucrose content, with a variation of 1s. for each ½% above or below that figure; the average cost to the factory, including carriage, was between 42s. and 43s. per ton.

Extraction of the juice.—The method most universally in operation for the winning of sugar from the root is that known as the diffusion process, according to which, by a systematic circulation of hot water through a battery of vessels containing finely shredded beet-roots, the crystalloids (sugars and salts) are caused to diffuse through the membrane of the plant-cells, leaving the colloidal constituents behind. Although this mode of extraction has been almost exclusively in use for fifty years, certain disadvantages associated with it are fully recognised, and recently modifications of it, if not, indeed, entirely new processes, have been described. Among the difficulties inherent in this form of extraction is the accumulation of large amounts of waste waters from batteries and from pressing the exhausted pulp. To reduce the water used in the factory is very desirable from every point of view, and a method of continuous extraction, on the counter-current principle, offers great advantages in this respect. A practical test of a system based on this principle, protected by patents taken out by K. Philipp,⁴⁸ has taken place in Germany during three campaigns,

⁴⁸ G.P. 269,691. 289,670.

and H. Danckwerts,⁴⁷ the manager of the Obernjesa factory in which it has been installed, has expressed the opinion that the new process provides a method well adapted to displace ordinary diffusion, its most notable advantages being: smooth working, economy of labour, absence of waste waters, and the comparative ease with which frosted roots may be treated. The installation was designed for, and actually operated 1500–1600 tons of roots per 24 hours. It consisted of three sections: (1) The chip-heating system; (2) the extractors, and (3) the control appliances for operating the plant. The extracting system was composed of a series of twelve rectangular troughs, six and a half feet in width, provided with stirrers. In practical operation, beet-chips of 3 mm. in thickness are introduced into a screw conveyor-trough and mixed with several times their weight of hot circulating juice at 92°–95° C., drawn from the extractors. In vigorous agitation, this mixture of chips and hot juice is conveyed to No. 1 trough of the series where the counter-current extraction begins. The chips are then passed from one section of the extraction troughs to the next, in contrary motion to the flow of the juice, by means of transfer stirrers and valves. When, by tests, it is judged that the juice is of proper strength, a portion is drawn off for heating the chips and the rest sent to the factory. By this apparatus, now known as the Philipp-Forstreuter, a juice of 15.5° Brix was obtained, leaving exhausted chips containing 16–17% of dry substance of which 1.5% was sugar; of this, however, half was recovered in the press water. A comparison between this method of continuous diffusion and that described as the "rapid" process patented by Paschen and described fully in a recent Report,⁴⁸ will show some similarities. This latter process, it may be remembered, was subjected to some criticism on various grounds, one of them being the low density of the resulting juice, *viz.*, 13.29° Brix, and the greater quantity of water that, in consequence, had to be evaporated. The figures quoted of the performance of the Philipp-Forstreuter apparatus seem to indicate an improvement in this respect, and the juice obtained appeared to be brighter and better in colour than that obtained from battery diffusion, and ran easily through the factory, working up eventually into a good massecuite. It will be interesting to observe the further development of this system.

The apparatus devised by J. I. Thornycroft⁴⁹ for the extraction of sugar by a system of continuous diffusion has already been described and favourably commented upon. A further improvement has been made by the inventor, which consists in increasing the cross-sectional area of the vertical diffuser in an upward direction. By this alteration more space is given at the top of the diffuser for

⁴⁷ *Deut. Zuckerind.*, 1923, **48**, 233.

⁴⁸ *Ann. Repts.*, 1920, **5**, 404–405.

⁴⁹ E.P. 195,462; *J.*, 1923, 558A.

the material (sliced beet) and in consequence there is less chance of the diffuser becoming choked.

These methods of continuous diffusion are but mechanical variations of a well established system of juice extraction not involving a departure from any recognised principle. In ordinary practice it is customary to avoid rupturing the cell-wall, for if that were done, the process would cease to be one of diffusion, and, by the consequent introduction of colloidal (pectinous) substances, the purity of the juice would be lowered, and difficulties in subsequent operations would arise. An examination, however, of the details of the new process of extracting sugar from beets, protected by H. Plauson,⁵⁰ reveals a complete departure from existing practice. Here it is proposed to subject the washed roots to the finest disintegration possible in a colloid-mill, in the presence of milk of lime. Owing to the fine state of division, chemical action is completed in a minute, and saturation with carbon dioxide may be effected in the mill at once. The carbonated juice is then filtered, under high pressure, through an ultra-filter press, a clear juice resulting and an exhausted residue, with a low water content, containing only small quantities of sugar, being left behind. As there do not appear to be published records of any trial of this process on the large scale, further consideration of it may be postponed.

Clarification.—The generally adopted method of defecating beet juice is by adding to it a thick milk of lime of about 20° B. at about 75°–80° C. and subsequently introducing carbon dioxide to precipitate the lime. No departure of any great importance from this well established system has been announced during the year.

In the preparation of the milk of lime, the last sweet water from the filter presses is frequently used. Attention was called by P. Beyersdorfer⁵¹ to the destruction of sugar that may here take place, amounting to 20% of that originally present, especially if the temperature on slaking exceeds 100° C. This subject has again been investigated by J. Vondrak⁵² in a series of factory and laboratory experiments. These showed that the purity of the milk of lime was practically the same as that of the sweet water from which it had been prepared, and its content of soluble calcium salts had only increased by a very small amount, whereas, had decomposition taken place, calcium lactate in appreciable amount would have been found. Vondrak is of opinion that Beyersdorfer's method of determining the sugar remaining in the scums gave results much too low. When an insufficient amount of sweet water is used for slaking the lime, a loss of sugar might occur and then may reach 13%.

⁵⁰ E.P. 190,314; *J.*, 1923, 155A.

⁵¹ *Ann. Repts.*, 1921, 6, 432.

⁵² *Z. Zuckerind. Czecho-slov.*, 1923, 47, 311; *J.*, 1923, 369A.

The action of lime upon beet juice has been studied recently by various chemists and the results very fully recorded.⁵⁵. The further experiments of V. Skola⁵⁴ are of interest as showing the composition of the precipitate formed by liming with 2% of CaO (1) in the cold ; and (2) at a temperature of 80° C. In the first case, the precipitate contained too much mineral matter and too little nitrogenous matter to render it suitable as a cattle fodder ; and, further, of the 2% of lime used, only 13% had been precipitated and 87% had passed into solution. When liming at 80° C. the precipitate obtained was considerably richer in nitrogen and phosphates. A reference to the previous work on this subject will show that proposals to defecate first with only a small quantity of lime, and to remove the resulting precipitate before proceeding to complete liming and carbonating, have not met with favour, one of the objections being the difficulty of filtering the slimy precipitate so obtained. Skola⁵⁵ has endeavoured, by various methods, subsiding, mechanical filtration, electro-osmotic drum filtration, and centrifuging, to overcome the difficulty, but without conspicuous success. It would thus appear from his labours in this field that neither cold defecation nor initial treatment of beet juice with small quantities of lime offers any advantage over the methods in general use. An interesting contribution has been made by H. A. C. Van der Jagt,⁵⁶ by a series of laboratory experiments in which he applies De Haan's well-known process of cane-juice defecation to the clarification of beet juice and compares it to the ordinary mode of practice in Holland. De Haan's method consists in adding lime gradually to the juice while carbon dioxide is simultaneously pumped through it, the reaction being maintained at an alkalinity not exceeding 0.3 g. of CaO per litre, while the temperature is not allowed to exceed 50° C. In beet juice, on account of the absence of "glucose," a higher temperature can be maintained without detriment, and therefore Van der Jagt's tests with this process were carried out at 80° and 90° C. From these it would appear that while single carbonatation, according to ordinary practice, results in an increase in purity of juice of 3.35%, single carbonatation by De Haan's method, at 90° C. results in an increase of 4.38%. These experiments are quoted here in confirmation of the advantages, previously referred to,⁵⁷ of producing within the juice a precipitation of calcium carbonate which, by virtue of its granular condition, increases the adsorption of the colloids. Notwithstanding that less lime is required by De Haan's method than by ordinary carbonatation, the mode of precipitation is favourable to adsorption.

⁵⁵ *Ann. Repts.*, 1920, 5, 406-407 ; 1922, 7, 403.

⁵⁶ Z. Zuckerind. Czecho slov., 1923, 47, 381.

⁵⁷ *Ibid.*, 1923, 47, 475 ; J., 1923, 847A.

⁵⁸ *Chem. Weekblad*, 1923, 20, 9.

⁵⁹ *Ann. Repts.*, 1920, 5, 407.

About two years ago, Ricard, Allenet et Cie. obtained protection⁵⁸ for a process for purifying beet juice by adding a soluble alginic acid and precipitating alginic acid or calcium alginic acid with lime. Details have now been published by E. Saillard⁵⁹ of large-scale trials of this process, made in France, and from these it is evident that while the tests were not unsatisfactory, the purity of the resulting juice, or the amount of nitrogenous matter precipitated, did not differ materially from the results obtained in ordinary practice. The filter-press work was adversely affected by the slimy nature of the precipitate. Apparently, therefore, this "Ginal" process, as it has been termed, possesses some disadvantages which, unless overcome, will militate against its general adoption.

In all processes of clarification of sugar juices, cane or beet, by treatment with lime and heat, it is of importance to point out that the major portion of the impurities, such as gums, pectinous and albuminous substances, are eliminated by action of heat and are adsorbed by the lime, forming a precipitate which settles out more or less readily. As the removal of these organic substances, colloidal in nature, by a direct, non-chemical method, would tend towards simplification of the process and improvement of the product, any claims in this direction put forward on behalf of a filter are naturally closely examined. Two filters, of this character, have recently appeared, the Plauson apparatus,⁶⁰ and the "stream-line filter" invented by H. S. Hele-Shaw.⁶¹ The latter has arrested considerable attention by its ability to yield clear and colourless solutions from dyes, milk, beer, and raw sugar solutions. Although it cannot be said that these filters are adequate to the technical requirements of the sugar industry, they are an advance on anything of the kind hitherto produced and are probably capable of considerable development.

DECOLORISING CARBONS.

Generally speaking, while much of the work on these products carried out recently has been valuable, it is probably true, as J. F. Brewster⁶² points out, that the methods of manufacturing these carbons have developed more quickly than processes for their successful application. The present price of good decolorising carbons is so high as to militate against their extensive use, and the aim of producers must accordingly be directed towards a reduction in the initial cost. The interest, therefore, attached to methods of manufacture largely centres around this point.

It cannot be said that any of the methods of preparation published

⁵⁸ E.P. 173,735.

⁵⁹ *Suppl. Ciras hebd.*, No. 1719 of 1922; *J.*, 1923, 196A.

⁶⁰ *Intern. Sugar J.*, 1921, 23, 680.

⁶¹ *J.*, 1923, 353T.

⁶² *La Planter*, 1923, 70, 471.

during the year under review differ in any radical way from those already well known and described, but allusion may be made to two methods of applying these carbons in sugar production for which protection has been obtained. In ordinary practice a small percentage of carbon is simply mixed with the hot sugar solution to be decolorised, and the mixture filtered through any well-known type of filter. Reference to a former Report⁶³ will shew that it was known that carbons are more effective in slightly acid solutions, and that J. F. Brewster and W. G. Raines had translated that acidity into terms of hydrogen-ion acidity. Their investigations have now developed into a patented process,⁶⁴ and it is claimed that by adjusting the hydrogen-ion concentration to an optimum for the liquor to be treated the most effective decolorisation is obtained. While the carbon is adsorbing the impurities, the p_{H} value should be 4, but, subsequently, it should be reduced, to avoid inversion, to 6 or 6.5 by partial neutralisation with alkali. Another mode of applying carbon to decolorise sugar solution is advanced⁶⁵ with the object of reducing the quantity to be used to a minimum. In this process, designed for use with beet juices, it is proposed to allow the comparatively small amount of carbon which is used to act in conjunction with other clarifying agents, like kieselguhr and wood-meal, and then subject the whole mixture to treatment with lime. After mixing the syrup (50°–60° Brix) with these materials, it is treated with sulphur dioxide or carbon dioxide at 90° C., until the alkalinity is reduced to 0.01% CaO. Good cakes and brilliant juice are thus obtained, the former containing the carbon being subsequently used in the juice at the first carbonatation.

Passing from these special methods to a consideration of the general application of carbons in sugar manufacture, it is possible from the experience now gained, and published in recent articles, to obtain a fair impression of the capabilities and limitations of this system of refining. The possibility of clarifying and decolorising cane juice, at one operation, by the addition of a small amount of carbon is very attractive, but has not yet been realised in general practice on account of the nature and amount of impurities which the carbon would thereby be called upon to adsorb. Experience has shown that in employing so expensive an agent, it is necessary before attempting treatment with the carbon, firstly to separate the sugar by crystallisation from the bulk of the gums and colouring matter, and secondly to subject the sugar so obtained to a washing (affination) process to bring it to the high degree of 99% purity. This is confirmed by the experiments of W. H. Dunstone⁶⁶ in Louisiana in attempting to deal with cane juice direct, and by

⁶³ *Ann. Repts.*, 1921, **6**, 429.

⁶⁴ U.S. P. 1,447,461; *J.*, 1923, 388A.

⁶⁵ C. Görlitz, and Lehmann u. Voos, G.P. 363,699; *J.*, 1923, 369A.

⁶⁶ *Facts about Sugar*, 1923, **16**, 190.

J. F. Brewster,⁶⁷ who, referring to the same mode of operating, draws attention to the large amount of carbon required in the process and the correspondingly large regenerating equipment.

This tendency in modern carbon processes to lessen the work to be done by the carbon to more or less of a finishing process is suggestive as indicating that the part carbons may play in refining is limited. The principal factor that governs this limitation is that of revivification or re-activation of the exhausted carbon. This is being fully realised by those well qualified to express an opinion. J. N. A. Sauer,⁶⁸ for example, in a very comprehensive article on "The care and revivification of Norit decolorising carbon," points out that the adsorbed organic matter when burned (in a revivifying plant) is transformed into extremely fine non-porous and non-active carbon, except when it is given special treatment to activate it. In addition to the organic impurities adsorbed, exhausted carbons may also contain inorganic matter, like calcium salts and silica, which may be present in the raw product dealt with, and it is remarkable how the latter can increase if a system of pre-filtering is not in operation. This recognition of the importance of revivification is welcomed, because it is only through this that expensive carbons can ultimately find a permanent place as refining agents.

ANALYSIS OF SUGAR PRODUCTS AND CHEMICAL CONTROL.

Determination of Reducing Sugars.—The two principal methods—the gravimetric and the volumetric—of determining invert sugar by its reducing action on copper sulphate, are both in common use, the former for more exact determination and the latter for routine work in sugar factory or refining laboratory. Unfortunately the results obtained by the volumetric method are vitiated by various influences, one of them being the ease with which the cuprous oxide is re-oxidised. As the common mode of titration requires the interruption of boiling for the withdrawal of a portion in order to test for unreduced copper with potassium ferrocyanide as an external indicator, the opportunity of back-oxidation is increased. The fact that methylene blue is completely decolorised in hot alkaline solutions by aldoses and ketoses has been made use of by L. Eynon and J. H. Lane⁶⁹ by employing it as an indicator in presence of Fehling's solution. They have shown that the end of the reduction coincides with decolorisation of the methylene blue and have outlined the best manner of making the titrations to ensure accuracy. In the analysis of all kinds of sugar products, honey, starch conversion products, malt worts, and beers, this modification of Fehling's volumetric method has been found convenient and expeditious and to give as exact results as those

⁶⁷ *Loc. cit.*

⁶⁸ *Intern. Sugar J.*, 1923, 25, 485.

⁶⁹ *J.*, 1923, 32T.

obtained by the gravimetric method. Besides the risk of re-oxidation while conducting titrations according to Fehling's method, other factors which adversely affect its accuracy have also been investigated during the year by Eynon and Lane.⁷⁰ These chemists found that the influence which salts of the alkaline earths exert on this determination is very considerable, but on the contrary, others, like magnesium sulphate and chloride, aluminium sulphate, ammonium chloride, potassium chloride, and normal lead acetate are without effect. A series of tests on different sugars disclosed the fact that the influence of calcium chloride solution was most pronounced on lactose, due probably to the fact that this sugar is less rapidly oxidised by Fehling's solution and, consequently, more time is given for the calcium salts to act upon the sugar. That these investigations and results have an important bearing upon the most common sugar analysis will be obvious, for most raw products (cane more than beet), syrups and molasses contain calcium salts, in some cases in considerable amount. These authors have found potassium oxalate to be the most effective precipitating agent, which confirms the opinion of others.

In the standardisation of saccharimeters several refinements in method are necessary to ensure accuracy. Amongst the points to be observed is the purity of the sugar used in ascertaining the 100° point of the instrument. It is well known that small quantities of invert sugar present in the sucrose, amounting to 0·005%, may be capable of causing an appreciable error, and, in consequence, various methods have been proposed for the determination of these small percentages. One of them, devised by A. Kraisy,⁷¹ has recently been subjected to critical examination by I. M. Kolthoff,⁷² who finds it difficult in application and inaccurate in result. This latter chemist prefers a modification of J. B. Sumner's colorimetric method,⁷³ using dinitrosalicylic acid, which, in alkaline solution, in presence of dextrose or levulose, is reduced to a red or orange compound, the sucrose present remaining unchanged. Two solutions are employed in this test, one containing the dinitrosalicylic acid and sodium carbonate and the other a 4*N* solution of sodium hydroxide. The operations of reducing the dinitrosalicylic acid and of matching the colour in a graduated colorimeter tube against a "blank" prepared from chemically pure sugar free from invert, must be carried out under unvarying conditions. The manner of test, as described by Kolthoff, is very simple, and it is stated that, provided the conditions which he stipulates are adhered to, the method is preferable to any volumetric one and gives accurate results.

Determination of Ash.—The work during the past year confirms

⁷⁰ *J.*, 1923, 143T.

⁷¹ *Ann. Repts.*, 1921, **6**, 437; *J.*, 1921, 315A.

⁷² *Archief Suikerind. Nederl.-Indië*, 1922, **30**, 867.

⁷³ *J. Biol. Chem.*, 1921, **47**, 5.

what has been clearly established in former years,⁷⁴ particularly with regard to the factor to be employed in correcting a sulphated ash. For long it has been recognised that the 0·9 factor is inaccurate, but considerable variations from this figure make it difficult to determine a more exact one. For example, Y. L. Pun and J. R. Withrow,⁷⁵ incinerating at 500° C., consider 0·65 to be the suitable factor; A. Brodie and J. M. Reynolds,⁷⁶ as the result of the examination of 250 samples in Hawaii, find an average figure of 0·79, U. S. Jamison and J. R. Withrow⁷⁷ suggest 0·66, while H. A. Cook⁷⁸ considers it impossible to recommend any definite factor for raw sugar. This latter chemist suggests 0·75 as the factor applicable to molasses, while J. F. Brewster's⁷⁹ figure would be 0·81 for molasses and 0·84 for syrup. It seems, therefore, as if this question might be considered one of several equally ripe for settlement by an International Commission of Sugar Chemists. There appears to be general agreement that silica dishes give results that are too low, and Whaley finds nickel dishes, for direct incineration, superior to silica and more rapid than when platinum dishes are used, and the results quite as accurate.⁸⁰ Jamison and Withrow⁸¹ made a number of experiments in porcelain crucibles; as compared with platinum ones, identical results were obtained in both direct incineration and sulphating methods.

Determination of Hydrogen-ion Concentration.—The extent of chemical control in sugar production has this year been widened by a greater recognition of the importance of hydrogen-ion concentration, at different stages of the process. In the brewing industry,⁸² and for water purification,⁸³ the determination of the p_h factor has been of value, and it is only natural that sugar chemists should ascertain its significance in sugar manufacture. Consequently, beginning in the corn syrup industry, its application has spread throughout. Investigators are agreed that indicators selected by Clark and Lubs give satisfactory results.

The work of Brewster and Raines⁸⁴ and that of J. Beobide in this field has been directed toward the control of the liming of the raw juice. The application is simple and the colours obtained on testing with the appropriate indicator are controlled by "buffer" solutions of graduated p_h values. If it be determined, for example,

⁷⁴ *Ann. Repts.*, 1918, 3, 114.

⁷⁵ *Facts about Sugar*, 1923, 16, 275.

⁷⁶ *Intern. Sugar J.*, 1923, 25, 102.

⁷⁷ *Ind. Eng. Chem.*, 1923, 15, 386; *J.*, 1923, 414A, 567A.

⁷⁸ *Facts about Sugar*, 1922, 15, 418; *J.*, 1923, 283A.

⁷⁹ *J. Assoc. Off. Agric. Chem.*, 1923, 6, 365; *J.*, 1923, 414A.

⁸⁰ *Loc. cit.*

⁸¹ *Loc. cit.*

⁸² *Ann. Repts.*, 1922, 7, 421.

⁸³ *Ibid.*, 1922, 7, 483.

⁸⁴ *Intern. Sugar J.*, 1923, 25, 88.

that a good clarification has been obtained with a titratable acidity of 0.25-0.5 c.c. normal per 100 c.c. of juice, with phenolphthalein as indicator, this would be equivalent to p_{H} 7. The colour which most nearly corresponds to this value is bromocresol purple, which indicates a value of p_{H} 5.2-6.8, and this indicator gives a sharper and more satisfactory end reaction than phenolphthalein. Thus, by experience in working with these indicators, a more exact determination of the dissociated acid is possible than by only testing with litmus or phenolphthalein papers. What is of value in the raw factory is also applicable to the refinery, and H. Z. Perkins⁸⁵ has reviewed the limits of hydrogen-ion concentration at the various stages in refining where control is most needed, viz., at washing-plant, blow-up tanks, and sweet water evaporators. Generally speaking, the degrees of ionisation within which safe working is possible lie between p_{H} 4.0 and 6.8.

No doubt these preliminary investigations in this section of control will be subject to review later, in the light of further experience, but meantime this mode of assessing reactions as those signify in sugar manufacture, offers to the scientific worker in factory or laboratory, a better medium of expression than has hitherto been available. It seems somewhat incongruous, however, to state that notwithstanding the possibility of accurate methods of chemical control, reports have come,⁸⁶ during the year, from different parts of the sugar world indicating that the more elementary and basic principles upon which sugar manufacture depends are not always fully recognised or practised.

Chemical Control Results.—The Java control figures for the crop of 1922, issued by the Chemical Department of the Java Sugar Experiment Station, and epitomised by H. C. Prinsen Geerligs,⁸⁷ are always instructive as showing the progress possible with scientific management. A comparison between these figures and similar ones obtained in Hawaii for 1922 season and compiled by E. T. Westly⁸⁸ is of considerable interest:—

| Cane— | | Java. | Hawaii. |
|----------------------------------|----------------|-------|---------|
| Sucrose | | 12.87 | 12.97 |
| Fibre | | 13.19 | 12.95 |
| Bagasse— | | | |
| Sucrose extraction by mills | | 92.9 | 96.98 |
| Purity in raw juice | | 84.6 | 86.84 |
| Purity of final molasses | | 32.0 | 38.75 |
| Lost in bagasse on 100—sucrose | | | |
| in cane | | 7.07 | 3.02 |
| Undetermined loss on 100—sucrose | | | |
| in cane | | 2.25 | 1.27 |

⁸⁵ *Intern. Sugar J.*, 1923, 25, 368; *J.*, 1923, 1191A.

⁸⁶ *Ibid.*, 1923, 25, 85, 409; *Facts about Sugar*, 1923, 17, 40.

⁸⁷ *Ibid.*, 1923, 25, 296.

⁸⁸ *Sugar News*, 1926, 4, 177.

Commenting upon the Java figures, Geerligs thinks it is a matter for congratulation that the purity of the final molasses is the lowest on the Java statistics, and when it is remembered that this is an average figure representing the work of 182 factories, it is an evidence of excellent work.

Westly is of opinion that the factor above all others determining good work is high purity in the juice delivered to the mill, a condition which most cane growers are doubtless endeavouring to obtain. In this connexion it should be said that the ordinarily accepted formula for calculating mill extractions, viz., sucrose in the juice per cent. of sucrose in the cane, does not fully measure the efficiency of the operation, on account of the influence of certain inherent conditions beyond the control of the mill management. These factors are the fibre in the cane, the sucrose in the cane, and the purity of the juice. E. W. Kopke⁸⁹ has frequently advocated the substitution of fixed constants for these variable elements, in order that a formula might be obtained, from which could be calculated the milling efficiency based on the extraction which would have resulted had the cane and juice been of standard or "constant" quality, or, in other words, the ratio of "accomplishment to possibility." A similar argument has been applied to the work of the boiling station. There is much force and logic in the contention, but the difficulty would be in the general acceptance of the proposal by Control Stations whose records, for a considerable number of years, have been based on the customary formulæ.

STARCHES AND GUMS.

Starches.—There does not appear to be very much of particular interest to report in this department of the carbohydrate industry.

In the manufacture and preparation of starch from grain or tubers, a process has been patented by A. Boidin and J. Effront⁹⁰ by which, it is claimed, the bacterial method of digesting the proteins of crude starches and amylaceous substances is improved. The materials treated are subjected to an acid fermentation which causes the nitrogenous matters to pass into solution, the remainder being used for making starch. In the course of the fermentation a special spored microbe is produced which may be isolated and utilised with advantage in the process.

In the industrial use of starch, a series of experiments has been conducted by J. Huebner and V. Malwin⁹¹ on the effect of metallic salts of starch and of soap upon the tensile and rippling strain of cotton. As regards starch, these investigators found that the

⁸⁹ *Sugar News*, 1921, 2, 577; 1923, 4, 108.

⁹⁰ E.P. 171,991.

⁹¹ J., 1923, 66T.

ripping strain is increased in the air-dry condition, and after drying at 100°C . respectively, but drying the cotton at 120°C . brings the value back to normal.

As regards analytical data and research on the nature of starch it will suffice to quote the following: A. R. Ling and W. J. Price⁹² have extended their method for the determination of starch in barleys and wheats, previously described,⁹³ to the determination of starch in potatoes. A series of similar tests was carried out and the curve for potato starch was found to be almost parallel with that obtained with barley starch, under standard conditions of hydrolysis with extracts of malt having different diastatic power, the only difference being that a larger amount of apparent maltose is produced in the case of potato starch. A comparison of twelve different methods for determining starch in flour and brans has been made by K. Alpers and H. Ziegenspeck.⁹⁴ All the methods are considered to suffer from disadvantages and some to give inaccurate results. The polarisation methods of Lintner and Belschner⁹⁵ and of Evers⁹⁶ are recommended for their simplicity, but the possible error in polarimetric methods is stated to be more than 3%.

With the view of ascertaining the conditions which exist when starch solution is added to a weak solution of iodine in chloroform, with and without the addition of potassium iodide, J. B. Firth and F. S. Watson⁹⁷ have carried out an instructive series of experiments. They have found that starch solutions will give an immediate blue coloration with iodine solutions in chloroform for concentrations higher than $N/1000$, and that a small amount of potassium iodide (0.192 g. per litre) increases considerably the amount of iodine transferred to the starch solution. In titrating a solution of iodine in chloroform, in contact with starch solution, with a solution of sodium thiosulphate, the starch solution is the first to be decolorised, whereas, in the presence of potassium iodide, the chloroform is the first to be decolorised.

A study of the paste characteristics of corn starches, particularly thin-boiling starches with varying amounts of alkali, has been made by C. E. G. Porst and M. Moskowitz⁹⁸ using the Bingham-Green plastometer.⁹⁹ Addition of alkali in processing thin-boiling starches gives firmer pastes until the starch is nearly neutral. Further increases of alkalinity causes the starch paste to be weaker,

⁹² *J. Inst. Brew.*, 1923, **29**, 732; *J.*, 1923, 1037A.

⁹³ *Ann. Rept.*, 1922, **7**, 428; *J.*, 1923, 48T.

⁹⁴ *Z. Unters. Nahr. Genussm.*, 1923, **45**, 163; *J.*, 1923, 903A.

⁹⁵ *J.*, 1907, 281.

⁹⁶ *J.*, 1908, 238.

⁹⁷ *J.*, 1923, 308T.

⁹⁸ *Ind. Eng. Chem.*, 1923, **15**, 166; *J.*, 1923, 322A.

⁹⁹ *J. Ind. Eng. Chem.*, 1921, **13**, 703; 1922, **14**, 49.

of smoother consistency and better spreading power, and changes the paste from opaque to translucent.

Amongst items of general information relating to starch products, may be mentioned the isolation by H. Kunz-Krause¹⁰⁰ of a solid non-volatile substance from commercial dextrin. This substance, named dextrinol, is stated to be a cyclic ester of myristic acid, and to it the characteristic odour of commercial dextrin is said to be due.

¹⁰⁰ *Ber. deuts. Pharm. Ges.*, 1923, 33, 149; *J.*, 1923, 792A.

THE FERMENTATION INDUSTRIES.

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CELEBRATIONS marking the Centenary of Pasteur's birth were held in Paris and Strasbourg during the last week of May, 1923, and naturally lead to some thoughts on the progress of the fermentation industries since the time of the illustrious pioneer who did so much to raise them from their former position of empiricism to a place among the scientific industries. The brilliant discoveries which formed the landmarks in the ordered development of his life-work are only a part of the debt which science owes to Pasteur; they form the basis of much of our present knowledge of fermentation and disease, but, more than that, they are the inspiration which has guided countless later workers. Horace Brown has testified¹ to the enthusiasm which his discoveries, opening vistas of fruitful investigation in place of the rather sterile dogmas of the opposing school, awakened in the minds of workers in the fermentation industries. Based on the conception of the vital importance of the activities of micro-organisms, he set the practice of fermentation on a sure foundation and his insight went far to indicate the direction in which his successors must look for further knowledge of its mechanism. He foresaw the discovery of enzymes and was alive to the importance of the reaction of the medium in which micro-organisms lived. Both these conceptions have from year to year gained in importance, and the latter is—now that finer methods for its measurement are a commonplace—becoming as wide in its applications as the all-pervading hydrogen ions are to biological processes.

Looking through the work published during recent years, one feels that the conception of the hydrogen ions is fast linking up isolated facts in fermentation and enzyme action and formulating explanations of many processes which were formerly only carried out in quite empirical ways. Not only is it offering explanation, but it is serving as the basis of methods for the improvement of technical processes. Most of these have come from the Continent, where the lager beer breweries offer a wider sphere for their employment than the top-fermentation concerns of this country. In the majority of top-fermentation breweries the broad outlines of the process are much the same as they were when Pasteur's ideas began to spread and show the reasons which had led brewers to their

¹ *J. Inst. Brew.*, 1916, 22, 267.

adoption on empirical lines. In many places the same plant is still in use, but without the knowledge of the biology and chemistry of these processes gained since Pasteur set investigators in the right direction it would have been impossible to modify and adapt them to the changed conditions which arose in 1914 with the rapidity and smoothness that actually were achieved.

Coming down to a survey of the literature published this year, the spread of M. H. Van Laer's process for the acidification of the mash, based ultimately on the view expressed by Pasteur of the fundamental importance of the reaction of the medium, is very noticeable on the Continent. The idea is by no means new and has been carried out for many years, generally by the development in the mash of lactic acid bacteria either by direct inoculation with cultures or by a rather haphazard process of natural infection. Van Laer's process, as described in many communications to Belgian publications and in a paper read before the Institute of Brewing,² is an elegant adaptation of the use of hydrochloric or sulphuric acid for the purpose. It is based on a preliminary neutralisation of any alkalinity existing in the mashing liquor, and afterwards a further addition in the mash tun itself of one of these acids until a hydrogen-ion concentration of p_{H} 5·0 to 5·5 is obtained in the mash. The reaction aimed at is that which will facilitate to the greatest extent the enzymic changes which take place in the mash tun and produce wort with a reaction as near as possible to the optimum for the coagulation of proteins in the copper and for a pure fermentation, producing beer sufficiently acid to resist bacterial infection but not acid enough to cripple the culture yeast.

Van Laer's paper before the Institute of Brewing was entitled "New Possibilities of Increasing the Brewer's Extract," and in it he showed the great financial advantages to be gained by the adoption of scientific principles in technical operations which hitherto had depended on mechanical improvements in milling and in extraction of the grist by means of mash filters and methods of that kind, to increase extracts. As long ago as 1900 Fernbach showed³ that the activity of amylase and peptase increased as the point of methyl orange neutrality was reached, and it is well known that the conditions prevailing in the mash tun are far from being those most favourable for the optimum activity of the enzymes. This is particularly the case if the brewing water be alkaline or if large proportions of malt substitutes be used, for either of these conditions will reduce the acidity of the mash and remove its reaction quite markedly from the optimum for the enzymes. The adverse conditions of the mash tun are more

² *J. Inst. Brew.*, 1923, **29**, 202; *J.*, 1923, 468A.

³ *Ibid.*, 1900, **6**, 110, 532.

particularly of importance in connexion with the changes brought about by the peptase and their bearing on the production of a wort sufficiently rich in yeast foods when alkaline waters or raw grain are used. The increased peptonisation leads to greater extract, one-third of the increase being due to solubilised nitrogenous substances and two-thirds to sugars derived from starch which would otherwise have escaped conversion since it was embedded in nitrogen-containing cells which only yield to proteolysis. The increase of soluble nitrogen in the wort may, under certain conditions, prove a valid objection to the process, and in this country, where the malts are modified to a greater extent on the floor than they are for the majority of lager breweries, the disadvantages may outweigh the gain in extract that might be possible. Generally, too, with well modified malts, the reaction of the mash will be nearer the optimum for the enzymes than is usual on the Continent, and to that extent the addition of acid to the mash, which would prove an extraordinarily difficult problem with the usual English mashing appliances, is less necessary. This, however, does not minimise the advantages that may be gained when a large percentage of raw grain is used or the liquor contains notable quantities of carbonates. The addition of acid, as the simplest method of treating such liquors, has indeed been practised to a small extent in this country for some time, but the work of Van Laer makes the process more exact.

Experimental results advanced by Van Laer show that, with what appear to be under-modified malts, an increase of extract of 5 or 6 lb. per quarter is obtainable over the extract from fine ground malt. These are extremely striking results, and if even a quarter of that were realised with well modified material the result would be worth the trouble of attaining it. The increase of extract obtained by peptonisation and neutralisation of the wort to the extent of about two-thirds of its alkalinity to methyl orange, to a pH of 5 to 5.5, is due to an increase in the percentage of maltose and of proteoses derived from the proteins rendered soluble. The relation of maltose to dextrin is, however, kept within desirable limits by adjustment of the mashing heats. The increase in nitrogen may amount to 50 or 60%, compared with that of normal worts from the same malt.

In the brewery increased elimination of nitrogen follows much the same proportion and leads to a considerably heavier crop of yeast. The nitrogen content of the finished beer is not excessive and does not overstep the limits generally considered as the maximum admissible for a stable beer. The nitrogen figure depends on the nature of the malt and the proportion of raw grain, and the degree of peptonisation may be made to vary with any particular case under consideration.

Van Laer's work also shows the great advantage to the stability of the resulting beer attained by an increase of the free acidity of the wort. He finds that the optimum for the organisms of "turned" beer is p_H 6.8, while that for the development of yeast is p_H 6.0, but any increase of the acidity is far more harmful to the development of *Saccharobacillus pastorianus* than of yeast, the former being incapable of reproduction in worts showing a greater free acidity than p_H 5.4. The worts he dealt with were not so acid as normal English all-malt worts, but the prevalence in English beers of the infection referred to is sufficient to show the importance of control on the lines he indicates.

Economic conditions have made a resort to raw grain more and more necessary, and much attention has been given to the technical and scientific aspects of its use, particularly on the Continent. In Germany the freedom of the mash tun has led to the "discovery" of the advantages which its employment offers, particularly in the form of refined grits or pure starch, advantages which have long been known and exploited in other parts of Europe and in America. Many papers have appeared in the German brewing press, from the pen of Windisch and others, on this topic.

From the experimental brewery at the Berlin Institute F. Schönfeld reports⁴ that improvements have been effected in beers brewed from malt and raw grain, so that they are now practically equal to all-malt beers, though the latter are still superior for dark lager. As the proportion of raw grain is increased an inferiority in fullness and flavour manifests itself, and the tendency in Germany, on account of the preference of consumers for all-malt beers, is for a smaller use of raw grain when commercial conditions permit. The lower percentage of nitrogen in raw grain brews results in smaller yeast crops and slower brightening. The paucity of proteins and silica in colloidal suspension gives less perfect flocculation and more powdery yeast; the various types of yeast also lose their marked individual characteristics and become more uniform. This tendency of lower gravity beers, particularly when chilled and filtered, to come down to a dead level is also marked in this country. In Berlin they find that even stock cultures are affected in the same way, even in the case of specially typical low-attenuating top-fermentation yeasts which frequently have to be grown in all-malt worts. The non-flocculent form is, on the other hand, better for assisting the keeping qualities of raw grain beers and does not entail such frequent changes of stock as was formerly the case. The flocculent character can be restored by carefully drying the yeast and using it in that state for pitching.

A. E. Berry has reviewed⁵ the sources of maize imported into

⁴ *Woch. Brau.*, 1923, 40, Nos. 42-47.

⁵ *J. Inst. Brew.*, 1923, 29, 219.

England, and described the general outcome of the manufacture of flakes giving an indication of the variation in extracts produced by flakes of varying degrees of thickness.

The influence of acidity in conjunction with alcohol on the stability of beer has been pointed out also by A. Bamberger.⁶ In this case the total, not the free, acidity has been considered. For a beer of 1040 gravity an acidity higher than 0·08% of lactic acid with an alcohol percentage of 4% are necessary to ensure stability. The alcohol is not sufficient in itself to protect the beer from the activity of bacteria.

L. C. Wilson has described⁷ a simple continuous method for the addition of the necessary quantity of acid to the mashing liquor, and gives the results of his experience in the use of mineral acid. He finds the treatment very beneficial in preventing bottle haze in chilled beer and in causing the sediment of matured beers to settle more firmly in the bottle. Flocculation and settlement of sludge on the coolers are also favoured, and the resulting beers are sounder.

In the annual report of the Lehranstalt at Berlin⁸ an account is given of the investigations of W. Windisch and P. Kolbach on acidity of the mash. They find that the production of a given degree of acidity in the mash entails the addition of far more than the calculated quantity of acid; whereas in the case of worts the results agree with those calculated. In the mash the extra acid is taken up by tertiary phosphates in the husk. A very curious finding is that the most acid worts furnish the most alkaline beers, thus apparently indicating that yeast does not prefer an acid medium but thrives best when it has produced the most suitable degree of acidity by its own fermentative activity.

F. A. Mason⁹ has shown that the development of the organism known as *Acetobacter R.*, which produces ropiness in beer and was described last year by P. Hampshire,¹⁰ is inhibited by the addition of lactic acid.

Starch.

Discussion of the methods for the increase of extract in the mash tun naturally lead to a consideration of the advances made in our knowledge of the constitution of starch and of the changes which it undergoes during conversion. Much of the pioneer work in this direction was directly derived from a study of mash tun changes in the classical work of C. O'Sullivan and H. T. Brown. More recently the knowledge of the constitution of the carbo-

⁶ *Woch. Brau.*, 1923, **40**, 92.

⁷ *J. Inst. Brew.*, 1923, **29**, 568; *J.*, 1923, **702A**.

⁸ *Woch. Brau.*, 1923, **40**, Nos. 42-47.

⁹ *Bull. Bureau Bio-Tech.*, 1923, 288; *J.*, 1923, **323A**.

¹⁰ *Ibid.*, 1922, 190; *J.*, 1923, **25A**.

hydrates has been greatly advanced by the researches of J. C. Irvine and his school. By processes of methylation Irvine¹¹ has produced stable methoxy compounds of the simpler sugars which have served as reference substances in his work on the constitution of the more complex starch, celluloses, and inulin. Starch was found to be built up entirely of glucose residues, and as a minimum the molecule must contain three glucose units arranged in such a way that one pair displays the coupling present in maltose, another pair having the coupling characteristic of cellulose.

Irvine advances some very suggestive ideas on the γ -sugars, which throw some light on the difficulties encountered in visualising the structure of starch and other colloid carbohydrates which may in reality be very labile and from their nature impossible to express in terms of the ordinary structural formulæ. He suggests that the stable sugars are not the forms which are primarily elaborated by plants or disrupted by animals, and the stable levulose is not the levulose that exists in combination in sucrose or inulin. This transient nature of γ -sugars is not inconsistent with enzyme results. Irvine speaks of fleeting glimpses of extraordinarily reactive sugars which in the process of artificial isolation rearrange themselves. They may, however, represent only a condition of the sugar molecule and not a chemical individual.

A. R. Ling and D. R. Nanji point out¹² that the incomplete knowledge of the constitution of starch is largely due to the failure of workers to recognise that starch consists of at least two constituents, each of which is attacked by malt diastase giving rise to products which are difficult to separate. Starch granules have long been known to consist of two components, which have been given different names by different workers—starch cellulose and granulose, α -amylose and β -amylose, amylo-cellulose or amylose and amylo-pectin, the former being completely converted to maltose by malt diastase and the latter giving a viscous paste when heated with water. Potato and arrowroot starch consist almost entirely of amylose and amylo-pectin, but other starches, as shown by D. H. F. Clayson and S. B. Schryver¹³ and by S. B. Schryver and E. M. Thomas,¹⁴ contain hemicellulose. Ling and Nanji find that barley, wheat, and rice starches contain notable quantities of these substances. In wheat, barley, rice, and maize starches the ratio of amylose to amylo-pectin is constant, namely 2:1, but the quantity of hemicellulose may vary widely.

In 1891 Lintner discovered isomaltose¹⁵ in wort and beer and as a product of the hydrolysis of starch by malt diastase.

¹¹ *Chem. Soc. Trans.*, 1923, **123**, 898.

¹² *Ibid.*, 1923, **123**, 2668; *J.*, 1923, 1239A.

¹³ *Biochem. J.*, 1923, **17**, 470; *J.*, 1923, 1088A.

¹⁴ *Ibid.*, 1923, **17**, 493; *J.*, 1923, 1088A.

¹⁵ *Z. ges. Brauw.*, 1891, 284; *Z. angew. Chem.*, 1892, **10**, 268.

English investigators have generally denied its existence on account of the use in their experiments of diastase preparations which hydrolyse both amylose and amylo-pectin and the difficulty of isolating isomaltose except as the osazone. By using dry precipitated barley diastase, which only converts the amylose, Ling and Nanji have been able definitely to show its existence among the products of starch conversion by malt diastase. Dry precipitated barley diastase produces from starch maltose and $\alpha\beta$ -hexa-amylose. Amylo-pectin when hydrolysed in presence of malt diastase at 55° gives 1 part of maltose and 2 parts of isomaltose. Isomaltose has $(\alpha)_D = 140^\circ$ and $R = 80$. Ling and Nanji, referring to Irvine's experiments, point out that he employed rice-starch, which may contain as much as 18% of hemicellulose, and as he deals with starch as a homogeneous substance rather than a complex of various constituents, it is difficult to interpret his results quantitatively. The ultimate products of hydrolysis which he obtained from methylated starch were a dimethylglucose and 2.3.6-trimethylglucose in the proportion of 2 : 1. Ling and Nanji point out that the major portion of the dimethylglucose must have been obtained from the amylose portion of starch, whilst the trimethylglucose was derived from the isomaltose unit contained in the amylo-pectin.

The ash of starch consists principally of silica and phosphate; the phosphate is possibly combined as an ester in amylo-pectin, and to this is probably to be ascribed the property of forming a jelly which is one of the characteristics of amylo-pectin. Ling and Nanji succeeded in separating the soluble part of the starch granule, amylose, from the insoluble amylo-pectin by keeping starch paste in a mixture of ice and salt for several hours. From the fibrous cotton-wool-like mass which is precipitated the amylose may be extracted by washing with water just below the gelatinising point of the starch, leaving the amylo-pectin undissolved. Amylo-pectin is converted by the action of the diastase of ungerminated barley into the α -amylo-dextrin discovered by J. L. Baker in 1902. This substance is not a dextrin, but may be regarded as $\alpha\beta$ -hexa-amylose.

Ling and Nanji consider that α -hexa-amylose, which is, according to Pringsheim, the primary amylose of the α -series obtained from starch by the action of *Bacillus macerans*, is the basal unit of amylose, and suggest a constitutional formula for it.¹⁷ A. Pictet and R. Jahn¹⁸ obtained a trihexosan, distinct from triamyllose and isotriamyllose, by heating starch with glycerol at 210°, and consider that its formation indicates that starch is a polymer of trihexose groups rather than a polymer of maltose anhydride.

On a general review of the literature, it would appear that starch has been treated by chemists as a substance of fixed composition, constitution, and properties, as any other carbon compound of the systematic science. On this view organic form, external structure, and organic actions are negligible. Similar treatment of the cellulose group is to be noted with similar results, in the methods adopted both investigating constitution and in interpreting their data. In the absence of a critical basis of investigation co-ordinate with realities, there has resulted an accumulation of research on secondary side issues, the records of which will disappear from the actual constructive story. This will be written in due time upon the comprehensive inclusion of all the factors of the problems presented by these natural substances of predominant importance, which are chemical, bio-physical, and, above all, industrial.

Until then, formulae of constitution and configuration are merely, or should be, short expressions of the results of destructive resolutions of varying intensity, with an indeterminate approximation to reality, the degree of approximation being inversely as the intensity of the conditions of reaction involved in laboratory investigation. Irvine's fleeting glimpses of the γ -sugars may have their application with double force to the parent substances. It may be that the groups which make up their very complex structure are so labile in their combinations that deductions based upon products of their degradation give fallacious ideas of their relations one to the other.

Enzymes.

In a paper on the hydrolysis of starch by salts, W. Biedermann¹⁷ brings forward some very striking results. It is generally held that enzymic changes are brought about by certain organic colloids which are identified as the enzymes themselves. When it was found that in certain cases the presence of another substance was needed, this was supposed to be secondary in importance and called the co-enzyme or activator. Biedermann has been led to attribute a greater importance to the substance which gives the enzyme its specific activity. This applies particularly to certain salts. It is notable that the salts are not only indispensable to activate the enzyme, but that they can alone hydrolyse starch. This is the case, for instance, with chlorides, bromides, and neutral phosphates. The presence of oxygen is essential, however, for the hydrolysis of starch by means of salts. Now Biedermann points out what seems the very extraordinary fact, that the other constituent of the complex which constitutes the enzyme, the organic colloid which is always thought of as the enzyme itself, cannot attack starch unless it is associated with the salt and with

¹⁷ Biochem. Z., 1923, 135, 282; J., 1923, 620A.

oxygen. One is almost driven to reverse the usual terminology and call the organic colloid the co-enzyme. The hydrolysis by salts is very much slower than that by diastase; it may, however, be hastened by mixing certain organic compounds, such as glycocoll or other amino-acid or albumose, with the salts. With albumose the conversion is very easy, like that with a dilute solution of diastase, and this suggests the possibility of preparing artificial enzymes. Biedermann considers that the hydrolysis of starch by inorganic salts can hardly be simply an action of the ions, because there is much greater need for the intervention of oxygen with salts than with diastase, and also because a much greater concentration of the salt is necessary to hydrolyse starch than when associated with diastase, in which case the minutest trace is sufficient to activate the reaction. In the complete absence of salts diastase cannot act.

Referring to the two constituents of starch, Biedermann considers that the amylo-pectin and amylose are not, as Maquenne suggested, in the relation of an outer layer to an inner kernel, but are intimately intertwined. A solution of amylose free from amylo-pectin may be obtained without difficulty by heating in water. Amylo-pectin completely separated from the amylose gives a brown colour with iodine.

It seems probable that the colloidal nature of the amylose plays an important part in the hydrolysis by salts. Its solution is a gel containing very highly dispersed particles of colloid. The oxygen may be adsorbed on these particles and act as an oxidising agent. The presence of oxidases in diastase must therefore be of considerable importance for the hydrolysis of starch, as the presence of oxygen is a factor which cannot be overlooked. Very dilute amylase solutions may be caused to give conversions arrested at dextrins, and this gives support to the idea that the degradation of starch goes through two stages, first giving dextrins which afterwards give rise to maltose; in fact, the presence of at least two enzymes can be demonstrated. Experiments with salts show that the production of maltose is much slower than that of the dextrins, and that it does not commence until the achromic point is reached. In any case, the whole of the amylose is never saccharified.

A parallelism exists also between the action of amylase and salts in relation to the reaction of the medium. The hydrolysis by salts only takes place in a perfectly neutral medium. Biedermann's researches have not yet arrived at the point when it can be decided whether the action of acid or alkali causes a modification of the organic matter which is considered as the support of the diastatic activator, or whether it acts by removing certain of the ions from the inorganic part of the diastase.

H. Pringsheim and W. Fuchs have described their recent work on the activators of enzymes,¹⁸ and distinguish between "co-enzymes," which are found mixed with the enzymes which they activate, and "complements," which have no biological relation with the enzymes to which they must be added to cause activity. Starch hydrolysis generally stops when about 78% has been converted to maltose, though, according to Maquenne, malt extracts activated with acid can completely convert starch. The complete hydrolysis of starch to fermentable sugars is of fundamental importance in distilleries, and the largest yield of alcohol is obtained by mixing the starch conversions, without any boiling, with yeast. The present authors find that the residuary substances left as the result of the degradation of starch by diastase are easily saccharified by the use together of diastase and yeast which has been liquefied by toluene. This yeast they call the "complement." It has not been definitely decided whether maltose is the only sugar formed in the diastatic hydrolysis of starch, and the presence of maltase in malt would lead to the suggestion that it may not be, but the present authors state that maltose is the only sugar present, and can be obtained in 100% yields from either ordinary or soluble starch by diastase and the complement. Lintner and Kirschner showed that dextrin could be transformed to maltose by the combined action of amylase and yeast, while taka-diastase degrades it to dextrose, but the residuary dextrin of the present authors is different from that of Lintner and can be freed from all traces of reducing sugars.

The researches of C. J. Lintner and M. Kirschner¹⁹ were directed to the determination of the nature of the ultimate dextrin obtained by the diastatic conversion of starch and to arrive at a decision as to the existence or otherwise of maltodextrins. They find that the final product of hydrolysis by diastase before maltose may be represented by the formula $(C_6H_{10}O_5)_nH_2O$, and is identical with Lintner and Dull's achroodextrin II. They consider that no product intermediate to this and maltose exists in purely diastatic conversions; that is to say, no maltodextrins are formed under these conditions. Any intermediate product found in beer must be formed by glycase.

The existence of maltase in malt has been much discussed. L. Maquenne shows²⁰ that malt extract is the seat of a continuous transformation which gradually raises the copper-reducing power and the same result, but to a greater degree, occurs in the presence of maltose. This is most easily explained by the conversion of maltose to dextrose, and malt extract must consequently contain

¹⁸ *Ber.*, 1923, **56**, 1762; *J.*, 1923, 858A.

¹⁹ *Z. angew. Chem.*, 1923, **36**, 119; *J.*, 1923, 322A.

²⁰ *Comptes rend.*, 1923, **176**, 804; *J.*, 1923, 1238A.

maltase. A. R. Ling and J. D. R. Nanji²¹ confirm the existence of maltase in malt which has not been too highly dried. Green malt contains considerably more maltase than kilned malt, and its presence in barley may be demonstrated by allowing ground barley to act on gelatinised starch paste, together with a little toluene, at 50° for 24 hours. The enzyme cannot be extracted by water from barley, and it is probably rendered soluble during germination. The power of the enzyme does not vary directly with the diastatic power of the malt as measured on the Lintner scale.

The determination of diastatic power is hedged about with many difficulties; different conditions of experiment and slight differences in reaction of the starch solution give rise to discrepancies in the results, and a recognition of this has led W. Windisch, W. Dietrich, and P. Kolbach²² to propose a method in which the p_{H} of the starch solution is maintained constant by the addition of a buffer solution of $p_{\text{H}} = 4.3$. The process differs from Lintner's too in that the diastatic power is measured by the amount of maltose extracted from 100 grams of malt determined iodometrically.

One of the greatest difficulties in the volumetric method for determination of diastatic power has been the recognition of the end-point in the titration of the Fehling's solution, especially in artificial light. This difficulty has now been got over by the introduction of methylene blue as an internal indicator. The introduction of this indicator by J. H. Lane and L. Eynon²³ for use in titrations with Fehling's solution has wonderfully increased the accuracy and precision of the volumetric determination of reducing sugars, placing it at least on a level with gravimetric methods, and to an equal degree it has made the volumetric determination of diastatic power more accurate.

The processes for the determination of diastatic power are not however, even with these new methods, made rigidly exact or comparable with what occurs in the mash tun. J. Effront showed that filter paper absorbs appreciable quantities of diastase so that the solution is appreciably less active after filtration. M. H. Van Eaer²⁴ finds that the diastatic activity of malt extracts which have been clarified by means of a centrifuge is 5% higher than that of the same solutions filtered. In the mash tun the enzymes are in the presence of large amounts of colloidal substances, and their activity cannot be considered apart from the insoluble substances which accompany them. Determinations on amyloytic activity

²¹ *Biochem. J.*, 1923, **17**, 591; *J.*, 1923, 1089A.

²² *Woch. Brau.*, 1922, **39**, 213, 219, 225; *J.*, 1922, 951A.

²³ *J.*, 1923, **42**, 32T.

²⁴ *Petit J. Braus.*, 1923, **31**, 1071.

should therefore, to be strictly comparable, be carried out under conditions similar to those existing in the mash tun. Faber observes²⁵ that amylase heated in contact with colloidal material is not destroyed or enfeebled in the same manner as in clear solution. It may even lose its activity temporarily, to regain it later on when diffused into the surrounding liquid, and this may explain why the practice incomplete saccharification is sometimes met with in malts whose diastatic power determined by the Lintner method seems satisfactory. Certainly the conversion in the mash tun and the resulting attenuation of the wort do not always agree with the diastase as determined in the usual methods; nor can this be wondered at when the nature of the materials the enzyme has to act on is compared with the purified starch used in the laboratory. Discrepancies in the determination may also easily occur through the use of differently prepared or unsuitable soluble starch. The supply must be of constant composition. In this connexion A. Reyhler²⁶ has given a survey of the many methods which have been proposed for its preparation, and suggests a new one in which an oxidising agent, potassium bichromate or permanganate, is used along with the acid.

The determination of the starch-liquefying function of diastase has always proved even more difficult and uncertain than that of the saccharifying. W. Windisch, W. Dictrich, and A. Beyer now propose²⁷ a method based on the liquefaction of amylo-pectin by malt extract. The amylo-pectin is prepared from wheat starch and acted upon by the malt extract under specified conditions of temperature and p_{H} . The liquid is then filtered and the filtrate hydrolysed by hydrochloric acid, the dextrose produced giving a measure of the amylo-pectin hydrolysed. The amount of starch liquefied by the diastase present in one gram of malt is taken as the liquefying power. The liquefying powers of malt bear no constant relation to their saccharifying power.

Yeast and Fermentation.

Fermentation activators continue to receive a considerable amount of attention. In particular, several investigators have studied the so-called " bios " of Wilder, but the discussion as to its actual existence can hardly be said to have yet arrived at any finality, nor does its relationship to the vitamins appear to be settled.

Yeast cells in very low concentration can either ferment sugar or to grow, but T. B. Heaton²⁸ finds that they may be induced to

²⁵ *Brass. et Malt.*, 1923, 13, 45.

²⁶ *Bull. Soc. Chim. Belg.*, 1923, 32, 221; *J.*, 1923, 672A.

²⁷ *Woch. Brau.*, 1923, 40, 49, 55, 61, 67; *J.*, 1923, 513A.

²⁸ *Biochem. J.*, 1922, 16, 800; *J.*, 1923, 158A.

do so by the addition of "bios." He considers that this substance may be a vitamin and has attempted to measure it by the rate of fermentation. He concludes that the substance which activates minimal concentrations of yeast is a definite chemical entity which may be measured fairly satisfactorily by the fermentation to which it gives rise, but that it cannot be identified with vitamin B.

M. B. MacDonald finds²⁹ that there is an increased growth in a sucrose mineral salt solution to which extracts of yeast have been added. His experiments indicate that yeast synthesises a substance which stimulates the growth of the culture to which it has been added. Wilder's "bios" is not a vitamin strictly so-called, being capable of synthesis by the yeast cell and not an indispensable nutrient material for yeast.

C. Funk and L. Freedman,³⁰ on the other hand, find that yeast hardly develops at all in a medium for which the sugar used has been first highly purified. They maintain that the factor B is not produced by the yeast unless a product containing the stimulating substance, called by Funk and Dubin vitamin D, is added.

E. J. Fulmer and V. E. Nelson³¹ examine the statement that yeast growth in a culture medium is due to a vitamin in the sugar. They effected growth in a medium in which a synthetic sugar, "methose," was used together with salts, making six successive sub-cultures; in these the number of cells increased in the proportion of 1 to 100,000,000,000.

Dealing with maceration juice or expressed yeast juice, H. Haehn and H. Schifferdecker find³² that cell-free fermentation is very favourably affected by the addition of boiled yeast juice, and they conclude that the constituents of the boiled yeast juice concerned are protective substances which inhibit the action of enzymes inimical to fermentation, protecting the zymase from endotryptase and the co-enzyme from lipase. The yeast from German breweries is said to contain more endotryptase than formerly on account of the use of raw grain, and in consequence the zymase in maceration yeast juice is more rapidly destroyed. This observation seems to open up a problem of considerable practical importance, and suggests another reason for the weakening of fermentation in raw grain worts in addition to those usually recognised.

H. von Euler and S. Karlsson endeavoured³³ to isolate and purify the activating substance described by Harden and Young. They found that the activity of fermentation varied with the amount of co-enzyme present and that the latter could be separated

²⁹ *J. Biol. Chem.*, 1923, **58**, 489; *J.*, 1923, 850A.

³⁰ *Ibid.*, 851; *J.*, 1923, 1145A.

³¹ *Ibid.*, 397.

³² *Woch. Brau.*, 1923, **40**, 175, etc.; cf. *J.*, 1923, 850A.

³³ *Z. physiol. Chem.*, 1922, **123**, 90; *J.*, 1922, 778.

to a great extent by dialysis. Obtained from an aqueous extract of yeast, it could be heated to 50° C. without much injury.

J. Orient found³⁴ that many amines activate fermentation in dilute solution, but inhibit it at higher strengths; some inhibit it at concentrations below that at which they activate it.

E. Lindberg prefers³⁵ to ascertain the activating value of extracts containing vitamins by determining their percentage content of vitamin B rather than by a yeast reproduction method. Water will eliminate co-enzyme from dried yeast to such an extent that dextrose is no longer fermented and auto-fermentation is also restricted.

R. Rigaux showed³⁶ that vitamins have a stimulating action on yeast production and act as a nutrient. The effect is more marked in a weak than in a strong wort. They are not indispensable to reproduction or fermentation, as amino-acids could act in a similar way; the yeast would then synthesise its vitamins.

Animal charcoal has also been found to act as a yeast activator by E. Abderhalden, who also shows³⁷ that the amount of glycerol formed in its presence during fermentation is greater than without, particularly in absence of air.

R. Willstätter, J. Graser, and R. Kuhn³⁸ have based a method for the isolation of invertase from yeast juice on the observation that it is precipitated completely from autolysed yeast juice which has been kept for some months. Its activity seems to vary with the content of organically combined phosphorus. Willstätter also refers³⁹ to an adsorption method for the isolation of invertase by which preparations 1600 times as active as the yeast from which they were prepared have been obtained. The invertase of autolysed yeast is much better adsorbed by alumina or kaolin if the solution containing it be first well diluted.⁴⁰

Yeast is generally held in high estimation as a source of vitamin B, but C. Kennedy and L. S. Palmer throw doubt⁴¹ on the correctness of this view. They consider that the efficiency of yeast in this respect is considerably less than is generally believed, but suggest that the vitamin content of young yeast cells may differ widely from that of mature cells. V. G. Heller also finds⁴² that the efficiency of dried yeast is lower than that of an equivalent of fresh yeast, owing to partial destruction during drying, and

³⁴ *Biochem. Z.*, 1922, 132, 352; *J.*, 1923, 113A.

³⁵ *Ibid.*, 1922, 132, 110; *J.*, 1922, 952A.

³⁶ *Petit J. Brass.*, Oct., 1923.

³⁷ *Fermentforsch.*, 1923, 6, 345; *J.*, 1923, 415A.

³⁸ *Z. physiol. Chem.*, 1922, 128, 1; *J.*, 1922, 952A.

³⁹ *Ber.*, 1922, 55, 3801; *J.*, 1923, 113A.

⁴⁰ *Z. physiol. Chem.*, 1922, 123, 181; *J.*, 1923, 66A.

⁴¹ *J. Biol. Chem.*, 1922, 54, 217; *J.*, 1923, 115A.

⁴² *Ibid.*, 1923, 55, 385; *J.*, 1923, 514A.

that the vitamin content of yeast grown in wort is greater than in a synthetic medium. He shows that yeast is capable of synthesising both constituents of vitamin B, the antineuritic and the growth-promoting.

The antiscorbutic properties of beer have been believed in for many years, and Captain Cook is said to have prevented scurvy by giving it to his crews. But this evidently applies to something very different to modern bright beer, which does not seem to possess any of the vitamin properties of yeast. Experiments have been made to find how far malt may contain vitamins, or whether any that exist in the green malt are destroyed during kilning. B. M. van Driel finds⁴³ by experimenting with guinea-pigs that malt dried below 60° C. contains none. J. Poenaru also found⁴⁴ that oxen fed on malt soon developed signs of malnutrition which could be got over by the addition of chopped straw etc. to their feed.

A. Tait and L. Fletcher have continued⁴⁵ their work on the development and nutrition of yeast, which was referred to in these Reports last year. Their use of malt rootlets as the source of the nitrogenous nutriment required by the yeast has been criticised, and they now advance the evidence which led them to adopt it after assuring themselves that there is practically no difference in the relative values of the nitrogenous constituents of rootlets and malt worts as a yeast food. Their investigations bear on the often-discussed question of the need for aeration during fermentation. They find that worts are sufficiently aerated by standing 48 hours to ensure normal yeast reproduction, and continuous aeration did not influence the rate of reproduction in their experiments. The retarding influence of carbon dioxide referred to by A. Slator is confirmed as well as the necessity of removing this during fermentation. The lag phase in the early stages of fermentation, they find, may be obviated by seeding with active cultures. These authors fail to confirm H. T. Brown's statement that during active reproduction the rate of yeast growth is a linear function of the time, and consider that the compound interest law holds good until multiplication ceases, but that the constant of growth rapidly decreases as the food supplies diminish and by-products increase. There is a marked retardation in the rate of reproduction in presence of 0.7% of alcohol together with the carbon dioxide produced; this is a much lower alcohol percentage than that generally accepted as being necessary to bring about retardation. In their experiments the alcohol formed and the yeast multiplication do not follow the same exponential law except in the very early stages of the fermentation. They show that direct counting gives the best criterion for

⁴³ *Woch. Brau.*, 1922, **39**, 258.

⁴⁴ *Intern. Rev. Agric.*, 1922, **7**, 858.

⁴⁵ *J. Inst. Brew.*, 1923, **29**, 509; *J.*, 1923, **792A**.

experiments on yeast reproduction. Variation in the weight of cells during fermentation precludes the use of the weight of final crops. The measurement of yeast reproduction and yeast growth is not always the same thing, as is pointed out by A. Slator.⁴⁶ Determined by counting cells, yeast reproduction is found to cease when the alcohol content reaches about 3%, but growth continues and an increase of 20% is often observed when the number has reached its maximum. Improved experimental methods in the investigation of the behaviour of yeast under anaerobic conditions show that absence of air does not prevent growth, but it is very restricted when compared with growth in presence of air. With small seedlings the yeast appears to draw something from the medium which allows a certain amount of growth in the entire absence of air; possibly both the yeast and wort may contain some substance which promotes anaerobic growth. A yeast extract was indeed found to promote growth under anaerobic conditions, but full growth was never obtained. In practical brewing the position seems to be as follows. The cells remain quiescent for a time before showing buds. Fermentation has then started and the saturation of the wort with carbon dioxide is sufficient to prevent yeast growth ever attaining its maximum velocity. Lack of air and the presence of carbon dioxide slow down the growth, and bubbling air through the fermenting wort promotes growth by removing carbon dioxide and supplying oxygen to the yeast. The number of yeast cells attains its maximum when the alcohol percentage has reached about 3%, after which they develop in size to the extent of about 20%.

• Many of the subjects already referred to are also under investigation at the Versuchs- u. Lehr-anstalt für Brauerei, Berlin, and its recently issued Report⁴⁷ summarises the work done there during the year. The activation of enzymes has been studied in connexion with the amylase of potatoes, which is found to be incapable of saccharifying soluble starch except in the presence of certain salts or amino-acids. These substances were themselves found to be capable of degrading starch under suitable conditions. H. Wentzell and R. Kolbach investigated the degree of dispersion of barley proteins in malting, mashing, and fermentation. By the aid of ultra-filtration they succeeded in tracing from the barley extract to the finished beer the proportions of high molecular proteins, albumoses, and amino-acids present.

Notes on other subjects dealt with will be found in the appropriate sections of this review. Among them are experiments on the acidification of the mash, on the use of raw grain, and on the preservative and bitter principles of hops.

⁴⁶ *J. Inst. Brew.*, 1923, **29**, 814; *J.*, 1923, 1145A.

⁴⁷ *Woch. Brau.*, 1923, **40**, 42, 47.

W. Windisch, W. Dietrich, and A. Mehlitz also describe⁴⁸ and discuss the separation of proteins of different types from barley by precipitation from the extract by means of stannous chloride, mercuric chloride, ferric acetate, uranyl acetate, and magnesium chloride and by fractional ultra-filtration.

THE INSTITUTE OF BREWING RESEARCH SCHEME.

Research workers connected with the fermentation industries are faced with very different problems to those generally met with in the more truly chemical industries. In the latter processes and methods have been built very largely upon laboratory investigations, and to a certain extent this is true in regard to the newer developments in fermentation, but such processes as those of brewing and wine-making have, after generations of evolution, taken on a more or less stereotyped form, and the schemes of organised research which have been set on foot are not directly intended to produce new products, nor are they expected to make revolutionary changes in methods. There are, however, so many unknown quantities in fermentation, in the materials used, or the conditions of treatment, that in no industry is research more needed. These unknown quantities also involve biological and chemical problems of peculiar difficulty; that connected with the constitution of starch, the most important raw material, has already been referred to. Many of the problems that await solution can be attacked in the laboratory, but there are others that can only be studied on the large scale in breweries. Such experiments are very costly, and it speaks well for the enthusiasm of brewery firms that several are found able and willing to bear the risks and cost involved. The Reports issued by the Institute of Brewing Research Fund Committee during the year show that a large amount of work on a technical scale has been done, and that the laboratories which are taking part in the scheme are not behind in progress made. The very complexity of the investigations makes progress necessarily rather slow, and perusal of the Reports shows how very essential is close co-operation between brewers, agriculturists, chemists, and biologists. Without a practical knowledge of the conditions and results on the large scale laboratory research is more than likely to prove of very little value.

The various schemes of investigation are mentioned here more or less in the order in which Reports on them have appeared in the *Journal of the Institute of Brewing*.

*Timber Investigations.*⁴⁹—These have been carried on partly in the laboratories of the Imperial College of Science and Technology,

⁴⁸ *Woch. Brau.*, 1923, 40, 1, 7, 13, etc.; *J.*, 1923, 284A.

⁴⁹ *J. Inst. Brew.*, 1923, 29, 351.

London, by Miss E. M. Thomas, under the direction of Professor S. B. Schryver, and partly in co-operation with practical men in the cooperages of breweries. It had already been found that satisfactory timbers were more permeable than unsatisfactory, and that the deleterious substances were extracted with greater difficulty from the latter during the usual seasoning processes. It was therefore decided to try various treatments with a view to find that which would best draw out these flavouring matters, neutralise them, or seal them in. In the laboratory treatment with alkali followed by acid gave promising results, but these hopes were not borne out by practical trial in the cooperage, and the research has not revealed any better method for the treatment of timber than those currently used, nor any method of making unsatisfactory timber useful. Some American oak is quite suitable for cask-making, and it has been found that suitable timber can be distinguished by chemical and physical tests from unsuitable timber, but in order to make use of the results obtained to select suitable timbers for market they must be studied at the place of origin of the wood in connexion with known varieties or kinds of oak.

Hop Investigations.—Two reports of the work carried out under the direction of F. L. Pyman, at the Municipal College of Technology, Manchester, have been issued during the year by the Research Fund Committee. In one of these, on "The nature of the preservative principles of hops,"⁵⁰ T. K. Walker gives a brief outline of work which has been done on the preservative principles of hops and an indication of the lines on which research is desirable. He calls attention to the conclusions of Bryant and Meacham and of Chapman that hop tannin has little precipitating power on the proteins of wort and has indeed very little significance in brewing. As the preservative power is generally considered to be associated with the soft resins, the investigators decided to make a close study of these very complex substances, and, by means of fractional crystallisation, separate, identify, and determine the properties of their constituents. When one considers the enormous difficulties faced in the analysis of resinous masses such as these, and the possibility that the preservative substance might be extracted from the hops in some other way than in association with the resins, if it actually resides in some such crystalline substance, as it is suggested, one wonders whether the method of attempting to extract it from the resins is really the most direct or whether some other way to attack the hops directly might not in the end be simpler.

However that may be, the investigators have succeeded in separating from the α - and β -resins respectively an α -acid, humulon, and a β -acid, lupulon, which have very considerable interest in that

⁵⁰ J. Inst. Brew., 1923, 29, 373; J., 1923, 736A.

they are only known to exist in the hop, and it seems possible that the unique value of the hop in brewing may be due to some constituents peculiar to it. It is therefore proposed to investigate these acids very thoroughly to determine their preservative action and the effect of the hydrogen ion concentration of the wort on their solution and surface tension effects, particularly in connexion with head-retention.

In Berlin, W. Windisch and P. Kolbach have carried out a research⁵¹ on the transformation of hop humulon when boiled in aqueous and alcoholic solution, in particular the influence of temperature, oxygen, and buffering. In the normal range of hydrogen ion concentration of wort the transformation of humulon depends on the amount of buffer substances present since these increase the solubility and therefore the degradation. This explains why low-gravity worts require longer boiling or stronger hopping than those of higher gravity to obtain the same degree of bitterness in the beer. The two degradation products, the α - and β -resins, were determined quantitatively. Experiments on the antiseptic properties of humulon and its products, and also in connexion with lupulon, are in progress.

In the second report on the "Extraction of humulon and lupulon and a new method for the estimation of the soft resins," T. K. Walker points out⁵² that none of the present methods for the determination of the resins can be considered as accurate; he suggests the use of methyl alcohol as solvent instead of those commonly employed, and describes a process in which it is used.

This laboratory investigation is complementary to the cultural and technical trials being carried out at Wye College and the East Malling Research Station and at several breweries. E. S. Salmon gives an account of the "Hop investigations, Wye College, 1921 and 1922,"⁵³ which shows how very important are the endeavours to breed new and improved varieties of hops of high preservative value and good flavour and at the same time immune to disease. The trials of the selected seedlings at the East Malling hop gardens are giving most encouraging results. In the "Sixth Report on the Trial of New Varieties of Hops,"⁵⁴ at East Malling, the same investigator describes the results obtained for the season 1922. Fifty-five new varieties have now become sufficiently established at East Malling for their distinctive characters to be ascertained. In all the classes, early, mid-season, and late hops, certain new varieties were preferred by the judges to any of the commercial varieties grown at the same station. Many of the new varieties also produced

⁵¹ *Woch. Brau.*, 1923, **40**, 42, 47.

⁵² *J. Inst. Brew.*, 1923, **29**, 379.

⁵³ *Ibid.*, 1923, **29**, 400.

⁵⁴ *Ibid.*, 1923, **29**, 879.

higher soft and total resins than the commercial varieties tested. These results testify to the value of the work being carried on at Wye and East Malling, and this is further shown by the desire of growers to obtain sets of certain of these varieties.

The growing trials are rounded off by investigations into the conditions governing hop-drying. These are described by A.H. Burgess in his report on the "Second Season's Work at the Experimental Oast, 1922."⁵⁵ The amount and proportions of the soft and hard resins did not seem to vary with alterations in the amount of sulphur used, with variations of temperature between 50° and 100° C., or with variations in air speed. Reck was found to occur if the initial temperature rose above 60° C., or if the air-current was too great.

Brewing Trials with Various Hops.—Not the least important of the investigations carried out under the auspices of the Institute of Brewing are the brewing trials with different varieties of hops that have been conducted at several well-known breweries during the last three years.⁵⁶ The brews were devised to determine the comparative brewing value of certain selected hops. The first year's work, with which the present writer was personally connected, was carried out at the brewery of Messrs. Barclay, Perkins and Co., Ltd., in London, and had in view a comparison between Tolhurst and Golding hops, the former being selected as a hop around which a considerable amount of discussion had arisen; it has very considerable attractions from a grower's point of view, but few from a brewer's.

During the second and third years the trials were extended to several other well-known varieties of hops and carried out independently at two breweries, Messrs. Barclay's and Messrs. Mitchells and Butler's, Birmingham. The results obtained were very concordant and are particularly valuable from the fact that the brews were made under normal trade conditions and with hops from two very different seasons' growth—the dry 1921 and wet 1922. Tolhursts proved very markedly inferior to all the other hops in preservative power in all three years. The climatic effect was most marked in the case of the Fuggles, which compared rather badly with Goldings after a dry year, but were equal to the latter in preservative power after the wet year. The low preservative power of the Tolhursts corresponds with a low percentage of resins; but that preservative power is not measured exactly by the soft resin content was proved by making brews with different hops, the hopping rates being so calculated that in each brew there was the same weight of soft resin per barrel. The keeping quality of these brews varied very greatly. If the preservative property of the

⁵⁵ *J. Inst. Brew.*, 1923, 29, 403.

⁵⁶ *Ibid.*, 1923, 29, 690; *J.*, 1923, 1038A.

hops is due to some constituent of the soft resin it would follow that that constituent does not bear a constant ratio to the weight of soft resins, and that it must be comparatively lacking in the Tolhursts, as that hop has an even lower preservative power than its low soft resin content would indicate.

The flavour of hops is a property of equal importance with preservative power, and these brews brought out several points in this connexion. The Tolhursts were found to be as lacking in flavour as in preservative power, and it was shown how difficult it is to determine from hand examination of a hop what flavour it would impart to beer. The Goldings were the best example of this. Although judged to be hops of delicate aroma, they imparted a very clinging bitter to the beer. Another interesting point in regard to flavour is the finding that the "acid" flavour of beer is not measurable by determination of the acidity by titration.

Neumann in the Lehranstalt Annual Report, states⁷ that his experiments show that the hard γ -resin is by no means the worthless ingredient generally supposed, its power of imparting bitterness to beer being 4, as compared to 10 for the α -resin, and 7 for the β -resin. Its discovery in the finished beer shows that, like the soft resins, it is able in part to withstand cooling, fermentation, and storage and to contribute to the bitter flavour of the beer. This means that in practice the risk of transforming the soft to hard resins by over-long boiling is not so serious as hitherto assumed. Moreover, prolonged boiling increases the degree of dispersion of the extractives and therefore their flavouring effect, thus reducing the consumption of expensive material.

It is interesting to compare these researches on hops with those being carried out in France. While in England the main lines of research are connected with a determination of the brewing value of different varieties and the improvement of existing kinds or the introduction of new varieties and with the search for the elusive preservative principle, the work of M. and Mme. Moreau in France has had in view the discovery of some objective characteristic by which the value of any particular sample of hops could be readily determined. For this purpose they propose to utilise the density of the cones. By measuring this property they are able to demonstrate the deterioration produced by the formation of seeds and confirm the Continental procedure of destroying all male plants in the hop gardens, though this is quite contrary to English experience, which shows that a small development of seed is necessary for complete development of the cones in this climate. Attention is also being paid to the raising of new varieties of hops from seed.

From an agricultural point of view one of the most important sides of investigations on crops is that dealing with the means of

⁷ Woch. Brau., 1923, 40, 42, 47.

extirpating pests and breeding immune varieties, and when the crop is as closely connected as hops or barley with the fermentation industries it becomes equally urgent for them. One of the difficulties encountered at East Malling was an outbreak of the "mosaic" disease, and this, as it affects the hops, is described by E. S. Salmon.⁵⁸ It appears to belong to the "virus" group, of which the commonest in this country are the "mosaic" and "leaf curl" diseases of potato. At present full methods of control are not available and cannot be hoped for before the exact nature of the disease and the manner of infection are known. These are being studied by V. H. Blackman and Miss Lacey. The East Malling trials showed that pulling the affected vines early in the season was unsuccessful as a treatment; they, however, suggested the very curious possibility that certain varieties of hops, e.g., M45, though themselves immune, may act as carriers. Experience in the East Malling Gardens seems to indicate that Fuggles are resistant. The identification of three hop diseases, apparently new to this country, is an indication of the constant watchfulness required to prevent the spread among crops of pests imported from abroad. These are the so-called "downy mildew," which has been brought from America or Japan, and is a potential danger to the hop crop. The other two are "hop leaf spot," caused by a *Cercospora* hitherto unknown, and "hop drop," which is liable to attack the vines after cold or wet, when the plants are in a weak state, causing the cones to fall off. These diseases are under investigation by E. S. Salmon and H. Wormald.⁵⁹

A very urgent problem is presented by the devastating effect that "smut" sometimes has on barley fields. It is so widespread that it is difficult to find seed entirely free from infection, and the discovery of some perfectly satisfactory method of disinfection is needed. The older pickling treatment with copper sulphate is now generally discredited, and a sprinkle with formaldehyde is recommended by E. S. Salmon and H. Wormald.⁶⁰ T. Bokorny, however, proposes⁶¹ a short immersion in a very dilute boiling solution of copper sulphate.

Barley.—In no direction are the interest and close co-operation of agriculturists in the researches of the Institute of Brewing more marked than in those connected with barley. It is recognised how closely brewing and agriculture are linked in these investigations, and nothing can make more surely for the prosperity of agriculture than that the farmer should be informed clearly and distinctly of what the consumer of his products wants. The brewing industry

⁵⁸ *J. Min. Agric.*, 1922, 29, 927.

⁵⁹ *Ibid.*, 1923, 30, 430.

⁶⁰ *Ibid.*, 1922, 29, 722.

⁶¹ *Brau. u. Hopf.-Zeit.*, 1923, 284.

is eager to increase if possible the proportion of materials available from British soils, and men eminent in the science of agriculture are co-operating in this direction. Among them the name of Sir John Russell stands out as chairman of the Barley Research Committee, which has issued a report on the first year's work.⁶² Under the title of the "Influence of Soil, Season, and Manuring on the Quality of Barley," it sets out the results which have been obtained after a most difficult season, climatically, for barley growing. It describes the variation in the crops from Plumage Archer seed grown at thirteen selected farms in various barley-growing districts of the country on five plots in each case treated with a series of artificial manures so made up as to determine the individual effect of each component. The complete fertiliser has increased the yield at each farm, but no very definite results have yet arisen from the manures in which one constituent was omitted, nor was that to be expected after one season's trials only, particularly when the season was so difficult. It is expected, however, that further years' investigations will show the value of the different ingredients under various conditions of soil, so that the farmer may be much more definitely advised than at present what types of manure to use. In general an increase of nitrogen in the manure resulted in poorer barley, but the quality of the crop was determined to a much greater extent by regional factors, conditions of soil, climate, etc.

The possibility of developing new varieties of barley, better suited than the present sorts to the maltster, the brewer, and the farmer, is being investigated at the National Institute of Agricultural Botany at Cambridge and elsewhere. The Department of Agriculture and Technical Instruction for Ireland reports⁶³ on the work of the Seed Propagation Department for 1922 in connexion with new varieties of barley in large- and small-scale experiments. Excellent crosses between Archer and Spratt and Archer and Goldthorpe have been obtained. In particular the "Spratt-Archer" has proved itself to be a considerable advance on Archer in both yield and quality. Research with a similar end in view is being conducted in France,⁶⁴ while at Dahlem, Berlin, one object of the trials is to find out what effect nitrogenous manuring in known amounts had on eight different races of barley.

Damp malts have for long been considered by English brewers as most detrimental to the quality of the resulting beer; but on the Continent and in the production of lager beer generally a much higher degree of moisture is tolerated. W. Windisch⁶⁵ considers

⁶² *J. Inst. Brew.*, 1923, **29**, 624.

⁶³ *J. Dept. Agric. and Tech. Instr. Ireland*, 1923, **23**, 86.

⁶⁴ *Petit J. Brass.*, 1923, **31**, 723, 800, 880.

⁶⁵ *Woch. Brau.*, 1923, **40**, 135.

that moisture *per se* is not detrimental, but during storage it will bring about spontaneously changes which completely alter the characteristics of the malt and lead to the production of beer of reduced stability and quality. Re-drying is not a cure, as it cannot restore qualities which have been lost during the defective storage, during which its diastatic activities have been re-awakened. M. H. Van Laer points out⁶⁶ that in some lightly kilned malts there may be 40—50% variation in the power of germination. During storage in a damp state proteolytic changes may therefore take place leading to the production of alimo-acids, which are basic as well as acidic, and may bring the reaction of the wort produced from the malt nearer to the neutral point. The diastatic activity of these malts is reduced and they are much more sensitive to any unfavourable conditions in the mash. It appears to be above all the diastase of the malt which suffers during defective storage.

H. M. Lancaster⁶⁷ states that his experience has led him to the conclusion that the conditions that make for the production of a diastatic malt from any barley are almost wholly decided by the character of the barley, and that the modifications that can be made by the malting process are small. If a barley of deficient diastatic potentiality is being dealt with, care must be exercised in the matter of kiln heats, and consequently the last 1—2% of moisture is not easy to expel.

PROPOSED NATIONAL INSTITUTE OF INDUSTRIAL MICRO-BIOLOGY.

All the schemes of research set on foot under the auspices of the Institute of Brewing Research Committee have a directly technical object connected with the brewing industry and with agriculture, and are concerned with a small part only of the problems which await solution in the domain of fermentation. Exhaustive study of these problems with satisfactory co-ordination of the various interests concerned would seem to be possible only through the formation of a central independent institute devoted to research and with facilities for the provision of specialised training. The establishment of such a National Institute of Industrial Microbiology was strongly advocated by A. Chaston Chapman at a joint meeting of the Biochemical Society and the London Section of the Society of Chemical Industry.⁶⁸ Contributions to the discussion by leaders in the various departments of the science of fermentation showed how wide was the field which awaited exploration, and what great advances in industrial chemistry might follow from

⁶⁶ *Petit J. Brux.*, 1923, 31, 930.

⁶⁷ *J. Inst. Brew.*, 1923, 29, 612.

⁶⁸ *J.*, 1923, 169T.

organised study of the activities of micro-organisms. The production of glycerol, aldehyde, citric and pyruvic acids, acetone, and butyl alcohol either from starch or cellulose was mentioned to exemplify what is being done, but owing to the lack of co-ordination in research a combined attack on any of the big problems calling for solution was rendered very difficult. Sir William Pope supported the plea for the foundation of such an Institute in the assurance that closer application to the study of the chemical activities of micro-organisms would lead to results of the utmost scientific and technological importance; it is indeed difficult to name one industry dealing with animal or vegetable products which is not intimately dependent on enzyme action and in which the nature of that enzyme activity has been sufficiently studied from the chemical side.

F. G. Hopkins suggested that if the permeability of the cell were modified, and if a greater number of species were utilised, the variety of products would be greatly increased, and A. Harden referred to the possibility of using dead instead of living micro-organisms, thereby greatly simplifying the operations involved. In agriculture micro-organisms are of the greatest importance, and Sir John Russell instanced ensilage and the breaking down of straw by bacterial action for the production of methane, hydrogen, or artificial manure.

ULTRA-VIOLET RADIATIONS.

For some years the beneficial effect of ultra-violet rays on yeast has been made use of at the Peroni Brewery, Rome, but unfavourable results have been obtained by some experimenters. To a large extent these unsatisfactory results seem to have been obtained through the use of yeast which had become altogether too feeble for satisfactory fermentation. Such yeast would be almost certainly killed rather than regenerated by the application of ultra-violet radiation, just as the unprotected bacteria are killed in Topley, Barnard, and Wilson's method⁶⁹ for obtaining pure growths from a single cell in bacterial cultures. The action of the rays is comparable to that of antiseptics. Applied to pitching yeast in a correct manner, it decides a selection, the weaker cells being destroyed while the more vigorous survive with even increased activity. P. Lindner confirmed⁷⁰ de Fazi's results on the acceleration of fermentation under the action of the rays, but pointed out that treated in thin layers and at rest the death of the yeast was likely to occur. A. Fernbach⁷¹ has therefore re-investigated the whole question at de Fazi's desire. The experiments on which the practical application of ultra-violet rays are based have been

⁶⁹ *J. Hyg.*, 1921, **20**, 221.

⁷⁰ *Woch. Brau.*, 1922, **39**, 166.

⁷¹ *Ann. Bras. Dist.*, 1923, **22**, 97.

repeated at the Pasteur Institute, Paris, and proved so successful in showing the increased activity of the treated yeast that practical trials were decided on and carried out at the Brasserie des Moulineaux, Paris. The procedure at the brewery was to mix the yeast to be treated with wort and cause it to run by means of a pump in a thin stream over a plate beneath a quartz mercury vapour lamp. The treated yeast was then used for pitching and gave uniformly better results than those obtained in a control fermentation with untreated yeast. Attenuation was increased, the head on the fermenting vessel and the foam on the finished beer were improved, and there was a more or less marked difference in flavour in favour of the treated yeast. The yeast cells also appeared to be more healthy when examined under the microscope, and in practice they retained through several generations the increased activity imparted to them. L'Incussen finds that diastase loses its activity on exposure to ultra-violet light, and that the destruction is greatest at p_n 4·6, the optimum for diastatic activity.

Reference has just been made to increased attenuation as an indication of the improvement of yeast; the importance of a sufficient fermentation and its bearing on the stability of beer is very generally recognised and was emphasised in a paper by C. G. Matthews,⁷² with special reference to the stability of summer brewings. Sometimes it is difficult to apportion the blame for defective fermentations between materials and yeast. Windisch considers⁷³ that there was some justification for supposing that the climatic conditions of 1921 were largely responsible for the frequent boiling fermentations noticed in worts made from that year's barleys. Kropff also reports⁷⁴ an instance of boiling fermentation which could be attributed to the malt alone. But in other cases change of yeast produced bad fermentations and defective attenuation from malts which had previously given normal results. In this case, however, the criticism might be offered that the defective fermentations were really due to decrease in the enzymic activity of the malt on storage. Windisch refers to complaints of insufficient primary fermentation with the malts made from 1922 barleys, and suggests that an explanation is to be found in incomplete degradation of proteins and a consequent coating of the yeast cells with minute particles which prevent transfusion. The low wort acidity from these particular barleys may be supposed to be the cause of the low proteolytic activity. G. M. Johnson attributes⁷⁵ the poor attenuations which have become more common of recent years to a selective action on the yeast through its continued use in low-

⁷² *Brewers J.*, 1923, **59**, 88.

⁷³ *Woch. Brau.*, 1923, **40**, 49.

⁷⁴ *Ibid.*, 1923, **40**, 55.

⁷⁵ *Petit J. Brass.*, 1923, **31**, 362.

gravity worts. The strongly attenuative yeasts have been gradually eliminated, and those yeasts best adapted to low-gravity worts and which produce little alcohol have become predominant. This selection of the less attenuative yeasts has also been favoured by the rapid fermentations generally used. The yeast which is thrown up most rapidly is that which attenuates to a lesser degree, and this has in many cases been taken for pitching. Yeast degeneration was felt most acutely in Germany during the war, when of necessity the worts were exceedingly weak. H. Dietsche states that a sudden change took place in the appearance of the yeast; it became black or grey, and had a very bitter flavour. He attributes the degeneration to the formation of a film of impurities on the cells with consequent prevention of the normal diffusion. In normal worts fermentation is sufficiently active to clean the cells naturally, and sufficient alcohol is formed to precipitate substances which otherwise would remain in a colloidal condition. P. Petit⁷⁶ discusses very fully the causes of and remedies for sluggish fermentations, and gives a method for removing these adhering colloidal films. Abnormalities of this kind were rather prevalent with worts from the 1922 barley malts.

Quite a number of very useful papers on practical subjects have appeared during the year in the *Journal of the Institute of Brewing* and other Journals; among them reference may be made to a few. "Carbonated Beer," by H. Abbot,⁷⁷ and also a series by the same author which has appeared in the *Brewers' Journal*, on a subject which the author characterises as unpopular, form a very comprehensive set of articles on a method of dealing with beer that is gradually gaining ground in this country for top-fermentation beers, as it had previously done in America for lager, and is doing at present on the Continent both for top- and bottom-fermentation. The appearance of beer is fast becoming a point of the highest importance in its manufacture, and there is no doubt chilling and carbonating well carried out lead to great improvements. There are several methods of chilling, and three of the most frequently employed systems are described⁷⁸ by A. Hadley, "Quick and Semi-quick Chilling"; P. K. Le May, "The Slow Chilling Process—Maturation and Chilling in Tank"; and "Slow Chilling—Maturation and Chilling in Cask," by H. Abbot. If appearance is gained by these chilling processes, they do not produce a beer that is very stable in bottle. Up to the present pasteurisation seems to be the only certain method which will produce a stable beer of this sort. The various methods of pasteurisation are described by Vogel,⁷⁹

⁷⁶ *Brass. et Malt.*, 1923, 13, 97.

⁷⁷ *J. Inst. Brew.*, 1923, 29, 8.

⁷⁸ *Ibid.*, 1923, 29, 958.

⁷⁹ *Brewers J.*, 1923, 59, 665.

and pasteurisation, together with the processes for the removal of the nitrogenous substances which are so inimical to stability, in a paper on the "Principles and Practice of Bottling," by H. L. Hind.⁸⁰ Head-formation is one of the most important properties which go to make the perfect beer, and one of the chief factors in it is the carbonic acid content of beer, which is the subject of a paper by J. A. Baker and H. F. E. Hulton,⁸¹ in which a method for determining the carbon dioxide in beer is described, together with the results of their determination of the change of carbon dioxide content during brewing and delivery of beer in tank to the retailer. The effect on the palate of decreasing saturation with gas is very marked, but the presence of gas is only one of the factors which goes towards the formation of head. Head-retention is equally important, and this subject has been discussed by the same authors,⁸² who have dealt very fully with the published literature in a valuable contribution which will serve as the basis for much further research on a subject which is as yet far from fully worked out. H. Freundlich⁸³ states that head-retention depends firstly on the colloids which permit of the formation of bubbles through lowering of the surface tension of the beer, and secondly on those that accumulate at the surface and render the walls of the bubbles viscous and tough, so that they do not readily collapse. W. Scott⁸⁴ has made a very notable advance in providing a means by which the head may be retained in cask beer when sent out for slow draught. It is based on keeping the cask, filled under pressure, with the bung underneath, so that no gas can escape round the shive, and providing a special tap for withdrawing beer as required.

Several papers on the 1922 season's barleys have appeared, and they should prove very useful in future years as a reference to the effect of a bad season on the crop and as a guide to malting and their subsequent treatment when similar wet years come round again. Those read before the Institute of Brewing were by H. M. Chubb and C. E. Sutcliffe,⁸⁵ and by J. Stewart.⁸⁶ W. Windisch⁸⁷ deals more fully with the worts and beers produced, and records the lower acidity of worts produced and the consequent importance of precautions to increase this when similar conditions arise.

Infection in the brewery has been dealt with by M. H. Van Laer,⁸⁸ and in regard to sarcina by H. Heron in a paper⁸⁹ in which he

⁸⁰ *J. Inst. Brew.*, 1923, **29**, 111.

⁸¹ *Ibid.*, 1923, 427; *J.*, 1923, 736A.

⁸² *Ibid.*, 1923, 747; *J.*, 1923, 1038A.

⁸³ *Woch. Brau.*, 1923, **40**, 23.

⁸⁴ *J. Inst. Brew.*, 1923, **29**, 735.

⁸⁵ *Ibid.*, 1923, 101.

⁸⁶ *Ibid.*, 1923, 228.

⁸⁷ *Woch. Brau.*, 1923, **40**, No. 14.

⁸⁸ *Brewers J.*, 1923, **59**, 665.

⁸⁹ *J. Inst. Brew.*, 1923, **29**, 281; *J.*, 1923, 803A.

describes very serious infection by *Pediococcus* in two breweries and the methods by which he was able to identify it and ultimately overcome the trouble.

The elimination of waste is one of the subjects of highest importance in all manufacturing concerns. The means by which it should be kept down to the lowest possible limit in breweries was the subject of a paper by W. A. Riley.⁹⁰ One source of waste is the liquor pressed from grains previous to drying. Attention has been drawn to the value of this liquor by H. E. Dryden,⁹¹ who also discusses the quantity of oil in the mash and in grains.

How far waste could be saved by the use of the centrifuge it is difficult at present to say. An article⁹² by L. Pierre on the different types of centrifuges and the selection of the most suitable in any special case is very useful in this connection.

"Brewing Waters"⁹³ is the title of a very useful book by C. A. Warren, dealing with the constitution of brewing waters and their treatment. The author draws attention to the value of magnesium salts in brewing waters—a consideration that is frequently overlooked.

A third edition of A. Harden's "Alcoholic Fermentation"⁹⁴ has appeared and testifies to the popularity of this volume of the series of monographs on Biochemistry.

• "The Action of Alcohol on Man,"⁹⁵ by E. H. Starling, is a critical scientific study of a subject which provides the *raison d'être* for the existence of the fermentation industries so far as they are concerned with beverages, and is a book of such authority that it must remain a standard work of reference in this connexion.

The tintometer has from its convenience and simplicity become the standard instrument for determining colour in brewing laboratories, but it has several defects which lead to discrepancies in measurement under diverse conditions. These largely depend on the fact that the glasses do not represent even approximately pure spectrum colours, and though a perfect match be obtained under definite conditions of light and concentration, it will cease to match if the source of light be changed or the depth of solution varied. This defect is particularly marked in places liable to fog, and the introduction of artificial illuminants with which sufficiently accurate and constant results may be obtained is very helpful. N. C. Beetlestone describes⁹⁶ how an electric globe may be used with

⁹⁰ *J. Inst. Brew.*, 1923, **29**, 538.

⁹¹ *Ibid.*, 51; *J.*, 1923, 286A.

⁹² *Brass. et Malt.*, 1923, **13**, 151, 166.

⁹³ *Brewing Trade Rev.*, London, 1923.

⁹⁴ Longmans Green, 1923.

⁹⁵ Longmans Green, 1923.

⁹⁶ *J. Inst. Brew.*, 1923, **29**, 61.

very satisfactory results, and shows that they compare very well with daylight determinations except with low colours, when the electric light gives readings 0.5° higher. The whole subject of colour determination is very ably discussed by H. R. Procter,⁹⁷ and a simplified accurate method for the determination of the colour of brown solutions described.

One of the less generally appreciated difficulties encountered in bottling, and particularly with pasteurised beer, is the precipitation of proteins by electrolytes dissolved from the bottle glass, which results in reduced stability and production of haze. A. Dizez⁹⁸ considers that it is due to negatively charged colloidal silicic acid from the glass. He recommends the use of hot dilute hydrochloric acid in the preliminary soaking of the bottles as a precaution.

It is sometimes necessary to prepare dried yeast for pitching purposes, and difficulty is encountered in the liability to autolysis. This has been got over by J. Raux and E. Bloch in a new process⁹⁹ in which the yeast is more rapidly dried by using plates of plaster of Paris. The product has a weight about 30% of that of the corresponding pressed yeast, and will maintain its fermenting power for at least two years.

In this country the mash filter has not made great headway, possibly one explanation being found in the fact that malt mills as generally made are not perfectly adapted to that process, and in consequence trials with the grists produced by unsuitable mills have led to rather disappointing results. The technique of mash-filter brewing and the adjustments required in the milling and actual mashing conditions are fully described by J. Raux¹⁰⁰ in a way that should prove very useful to intending users of the filter.

The production of *n*-butyl alcohol and acetone by fermentation of carbohydrate material is a comparatively new industry, and hitherto not much attention has been given to the recovery of the gaseous products of the process. How important it is to consider these products may be gathered from the statement of E. W. Blair, T. S. Wheeler, and J. Reilly¹⁰¹ that from 30 tons of maize as much as 295,000 cubic feet of gas is evolved in 36 hours, and they describe a method whereby 80,000 cubic feet of pure hydrogen or even more can be obtained from it.

PLANT AND PROCESSES.

The possibilities of filtration on a technical scale have been enormously increased by H. S. Hele-Shaw's introduction of the

⁹⁷ *J.*, 1923, 73t.

⁹⁸ *Bull. Ass. Anc. Elèves Louvain*, 1923, 2, 38; *J.* 1923, 674A.

⁹⁹ *Brass. et Malt.*, 1922, 12, 292; cf., *J.*, 1923, 197A.

¹⁰⁰ *Brass. et Malt.*, 1923, 13, 230, 247.

¹⁰¹ *J.*, 1923, 236t.

"stream-line filter."¹⁰² It dispenses entirely with pulp or any other material through which the liquid to be filtered is passed, and makes use of sheets of impervious paper packed together under pressure and held in a suitable casing. The sheets are pierced with two sets of holes forming a series of tubes through the pack. The liquid to be filtered enters through one set of tubes and passes between the individual sheets of paper, leaving all solid matter where it enters round the walls of these channels, and passes out by the other set of tubes. No application seems yet to have been made to the fermentation industries, but the requirements of the bottling departments of breweries would seem to call for an examination of the feasibility of its use and possible superiority to pulp filters. It might also prove suitable for the separation of yeast and for other purposes in the brewery itself.

Stainless steel is a material with very great possibilities in the construction of brewery vessels, but at present rather ruled out of court on account of its high cost. J. H. G. Monypenny¹⁰³ deals with the conditions which govern its resistance to attack by liquids. Water and vinegar have no action on it.

E. Willemart describes¹⁰⁴ a new digestion mashing process by which the mash is conducted in a closed copper-lined iron vessel capable of withstanding a pressure of 1 atm. and fitted with draw-off taps on different levels for the clear wort. It also contains a Weigel propeller and the necessary fittings for water and steam. Mashing is commenced at 18° C., and after 6 to 16 hours the clear supernatant liquid is drawn off. The thick mash is then diluted and mashed successively at 50° and 70° and boiled. After cooling to 70° the clear wort drawn off is returned to the mash. It is claimed that the gain in extract is very marked.

WINE, CIDER, AND OTHER BEVERAGES.

In the opening paragraphs of this Report reference was made to the enthusiasm with which Pasteur's discoveries were received in the brewing industry and the immense influence they have exercised since his day. Though the debt of viticulture to Pasteur was perhaps even more direct in that it owed to him its rescue from the devastating effects of silk-worm disease, wine-making is still much behind distilleries, breweries, vinegar breweries, and dairies in the application of his principles, and wine suffers from the failure to make use of pure culture fermentation in stability and in that the ordinary qualities have not all the *finesse* that they might possess. There are no doubt many difficulties in the application of pure fermentation to wine, but E. Barbet has

¹⁰² Proc. Roy. Soc., 1923, A 108, 856; J., 1923, 354T.

¹⁰³ Faraday Soc., April, 1923, J., 1923, 457A.

¹⁰⁴ Petit J. Brass., 1923, 31, 719.

shown¹⁰⁵ how it can be carried out with great commercial advantage and the production of wine that has much improved quality and keeping properties. A. Jarraud has described¹⁰⁶ a method by which wine could be aged by means of electrolysis, which causes an oxidation and brings about changes in wine comparable to those which occur during natural maturation. In three months white wines have apparently aged three years; bottled then they taste after six months like wines ten years old.

The manufacture of cider is still almost entirely in the hands of small concerns, who find it impossible to make use of refrigeration methods which would greatly increase the regularity and quality of the product.

C. Lambert¹⁰⁷ deals with this aspect of cider-making very fully, pointing out the advantages that would be obtained if through co-operation refrigerating machinery could be installed for cold storage of fruit, for the fermenting rooms, and for bottling with gas. Transport could also be greatly improved by the use of ice and more particularly by concentration of cider by freezing, a process which permits of the production of a concentrated juice which can afterwards be diluted for sale.

The work of the fermentation laboratory and cider brewing station at Ettelbruck, Luxembourg, is described¹⁰⁸ by J. P. Wagner. It is devoted chiefly to research work dealing with simple processes for the manufacture of beverages from native fruit, and prepares cultures of suitable yeasts for distribution to farmers.

C. T. Symons¹⁰⁹ describes the production of arrack in Ceylon from the juice drawn from the young inflorescence of the coconut palm. The Government has a model distillery, and the analyses of the spirit produced show an improvement over the native product, particularly in the copper content.

CELLULOSE FERMENTATION.

Two papers have appeared on the direct bacterial fermentation of cellulose, dealing with the large-scale experiments carried out by Power Spirits, Ltd., at Epsom. The first¹¹⁰ is a very general review of the subject and the possibilities of direct fermentation, by H. Langwell and H. Lloyd Hind, in which also the possibilities of its application to certain of the by-products of brewing, grains and spent hops, were mentioned. The second¹¹¹ formed part of a discussion at the Society of Chemical Industry,

¹⁰⁵ *Ann. Brass. et Dist.*, 1923, 22, 106.

¹⁰⁶ *Ibid.*, 1923, 105.

¹⁰⁷ *Ibid.*, 1923, 77.

¹⁰⁸ *Intern. Rev. Agric.*, 1922, 13, 629.

¹⁰⁹ *J.*, 1923, 252T.

¹¹⁰ *J. Inst. Brew.*, 1923, 29, 302.

¹¹¹ *J.*, 1923, 280T.

and was presented by A. H. Lynn and H. Langwell; in it the course of the experiments and their results¹¹² were dealt with in greater detail. The fermentation can be controlled to produce either alcohol or acetic acid at will. The results already obtained indicate that the fermentation of cellulose is likely to be an important industry in the near future. The direct fermentation process can deal with annual growths such as straw, without any preliminary treatment other than softening by steam alone or with a small amount of dilute acid which enables the material easily to be broken down into a pulp.

Sir Frederic Nathan referred¹¹³ to the production, as the result of fermentation, of methane, which offers possibilities in connexion with the synthetic production of formaldehyde and methyl alcohol.

In the course of the same discussion H. B. Hutchinson referred to the investigations he had carried out in conjunction with E. H. Richards at Rothamsted on the bacterial treatment of straw, which had developed into a commercial method for the production of artificial manure from vegetable refuse.

C. Neuberg¹¹⁴ has shown that acetaldehyde is an intermediate product in both the hydrogen and methane cellulose fermentations. Mme. Y. Khouvine has examined¹¹⁴ the cellulose-fermenting organisms (*Bacillus cellulose dissolvens n.sp.*) from the intestines, and finds that as the purity of the culture increases so its activity decreases. This can be corrected by the addition of an extract of horse manure to the cultures, and the author concludes that the organism requires its nitrogen in a degraded form.

For resistant celluloses, wood waste, and the like, saccharification processes are more suitable than direct fermentation. H. Terrisse and M. Levy¹¹⁵ improve on their original patent by drying the sawdust etc. to 5% water before treatment with hydrochloric acid solution. The material remains powdery and the acid recovery is simpler. The process is modified to be continuous. E. C. Sherrard and W. H. Gauger find¹¹⁶ that small quantities of certain mineral salts, such as mercuric chloride, cobalt nitrate, zinc sulphate, ferric sulphate, and magnesium sulphate give rise to increases in the amount of alcohol obtainable from a given amount of sawdust when used in conjunction with the sulphuric acid in the saccharification process. Preliminary treatment of the sawdust with 1% caustic soda solution was found to retard the formation of fermentable sugars, while chlorination followed by treatment with sodium sulphite inhibited it.

¹¹² J., 1923, 279T.

¹¹³ Biochem. Zeits., 1923, 139, 527; J., 1923, 993A.

¹¹⁴ Ann. Inst. Pasteur, 1923, 37, 711.

¹¹⁵ E.P. 186,139; J., 1922, 910A.

¹¹⁶ Ind. Eng. Chem., 1923, 15, 63; J., 1923, 286A.

FOODS.

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DURING the year under review no outstanding advance has been made in any department of food chemistry, although a number of papers of considerable interest have been published, ranging over a wide field.

VITAMINS ETC.

The mechanism of the formation of vitamins in plants has been further investigated by Miss K. H. Coward,¹ who has examined the conditions under which vitamin A is produced. She concludes as a result of her experiments that the essential factor is light, and that neither carbon dioxide, oxygen, chlorophyll, nor calcium salt is necessary for the purpose. The light, moreover, may be of long wave-length, and need not contain ultra-violet rays. These observations would seem to narrow the issue considerably, as hitherto chlorophyll has been considered to be an essential factor in the formation of vitamin A. Possibly, after all, the yellow colouring matters or lipochromes of plants, carotene, xanthophyll, and the fucoxanthin of sea-weeds, may be the active agents. Drummond in 1919 prepared pure crystalline carotene from carrots, and found it to be completely lacking in growth-promoting power, so that carotene itself is not a vitamin.² Several investigators have shown, however, that a certain parallelism exists between carotene content and vitamin content in plants, and Miss Coward has now shown that some lipochrome is always associated with the vitamin in plant tissues.³

We are still without definite indications as to the chemical nature of vitamins, but an interesting piece of work by K. Takahashi and K. Kawakami⁴ seems to bring us nearer to a solution of the problem. These investigators, starting with 1 kg. of cod liver oil, removed the fatty acids by saponification, and the cholesterol by means of digitonin, and subjected the residual syrup, after solution in a small quantity of methyl alcohol, to a temperature of -20° C. They thus obtained about 1 gram of a semi-crystalline product, containing carbon, hydrogen, and oxygen,

¹ *Biochem. J.*, 1923, 17, 124; *J.*, 1923, 417A.

² *Ann. Repts.*, 1921, 6, 476.

³ *Biochem. J.*, 1923, 17, 145; *J.*, 1923, 417A.

⁴ *J. Chem. Soc. Japan*, 1923, 44, 590; *J.*, 1923, 904A.

but no nitrogen, which they considered was almost pure vitamin A. It appeared to be of an aldehydic nature. A mouse at the point of death owing to lack of vitamin A was restored to health by being given 0·08 mg. of this substance daily for a period of 10 days. Previous experience of the claims of investigators to have isolated vitamins makes one chary of accepting these statements without further examination. Vitamins have been shown to be readily adsorbed by, and carried down with, other substances, and it remains to be seen whether the growth-promoting qualities of this substance are retained or gradually lost when it is further purified by recrystallisation.

The action of light as an auxiliary factor in the promotion of growth has been the subject of further experiments carried out in Vienna and London, and definite evidence has been obtained that air which has been irradiated by the light from a mercury-vapour quartz lamp is capable of producing prolongation of normal growth in rats on a diet deficient in fat-soluble vitamins.⁵

J. Effront⁶ has examined the absorption of pepsin by various substances, and finds that this enzyme may be separated to a great extent from accompanying proteins and other nitrogenous substances by absorption on paper pulp. The absorbed pepsin contains only 0·4% of nitrogen, and is five times as active as the original preparation. Effront concludes from this that pepsin is not of a protein nature and may be entirely free from nitrogen.

MILK AND DAIRY PRODUCTS.

The determination of the freezing point as part of the routine examination of milk appears to be established in America, and an apparatus termed the "Hortvet" cryoscope is to be found in many laboratories concerned with dairy products. In this apparatus the necessary reduction of temperature is obtained by the evaporation of ether in a vacuum flask, and it is stated that not more than 10 — 15 c.c. of ether is lost by evaporation in each determination. It has been shown by many workers that the freezing point is the most constant property exhibited by milk, and that, provided that the milk be not sour, this method furnishes reliable information in cases of watering. The determination of the correct freezing point of milk is a matter of considerable difficulty, necessitating elaborate precautions in order to avoid the errors due to supercooling and to the occasional formation of an ice film on the inner surface of the vessel, both of which tend to make the observed freezing point too low. In the Hortvet cryoscope these errors are liable to occur, but by working always in the same way the results obtained are comparable one with another,

⁵ E. M. Hume and H. H. Smith, *Biochem. J.*, 1923, 17, 364.

⁶ *Monit. Sci.*, 1923, 13, 7; *J.*, 1923, 287A.

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although the actual figures are probably from 0·015° to 0·020° too low. The freezing point of a solution of 7 grams of cane sugar in 100 c.c. of water at 20° C. is given by the Hortvet cryoscope as -0·422°, whereas the value given by F. M. Raoult,⁷ corrected for supercooling, is -0·409°, a difference which would correspond to about 3% of added water. Exact determinations could no doubt be made with the Hortvet cryoscope if the freezing point of milk were compared, under identical conditions, with that of a standard solution of cane sugar of approximately the same osmotic pressure, both values being then corrected for supercooling by comparison with the very accurate determinations made by Raoult on cane sugar, but for practical purposes the error referred to above may not be of great significance. It is pointed out in a pamphlet dealing with standard methods of milk analysis that a tolerance of 3% may be allowed in calculating the results, but this appears to be based on the natural variation observed in the freezing point of milk, rather than on the presence of a constant supercooling error.

The freezing point method appears to be finding favour also in Germany, Holland, and Switzerland. Gronover⁸ gives results obtained by it, but here again it would seem that the error due to supercooling has been neglected.

The so-called "simplified molecular concentration constant" of milk, introduced by L. Mathieu and L. Ferré,⁹ which is a figure based on the percentages of lactose and chlorine, is the subject of a critical study by C. Porcher.¹⁰ This figure is stated never to fall below 70 for genuine milk, and to furnish a reliable indication of watering.

The pasteurisation of milk by electrical heating is carried out in America by means of the "Electropure" process.¹¹ The milk is passed upwards between carbon electrodes embedded in opposite walls of a hard rubber composition material which is in turn fixed in a rectangular upright metallic box. The passage of the current between the electrodes rapidly raises the temperature of the milk to 165° F. (74° C.), after which the milk flows out continuously to the cooler. It is stated that milk treated in this way does not develop the "cooked" taste which is liable to occur when milk is pasteurised in the ordinary way. This process is very much the same as the one introduced several years ago at Liverpool by J. M. Beattie and F. C. Lewis, and which was the subject of a report by the Medical Research Council in 1920.¹² Being a "flash" process it could not be used in this country for the production of pas-

⁷ Z. physik. Chem., 1898, 27, 617.

⁸ Z. Unters. Nahr. Genußm., 1923, 45, 18.

⁹ Ann. Faclif., 1914, 7, 12.

¹⁰ Ibid., 1923, 16, 16; J., 1923, 286A.

¹¹ F. W. Robison, Ind. Eng. Chem., 1923, 15, 514; J., 1923, 621A.

¹² Special Report Series (No. 49) of the Medical Research Council, 1920.

teurised milk, unless the milk were subsequently held at 145° F. for half an hour.

Owing to the occasional use of hypochlorites for sterilising utensils used in dairy work, milk is liable to be contaminated with traces of chlorine compounds. P. Rupp¹³ has investigated the extent to which hypochlorites can be detected in milk, and has found that by means of potassium iodide and starch it is possible to detect 1 part of available chlorine in 50,000 parts of milk. The test, however, is less sensitive if the milk has been kept for any length of time at the room temperature, and at best it would seem capable of furnishing definite indications only in cases of comparatively heavy contamination.

A useful conference on the pasteurisation of milk was held at the Guildhall on November 21st, under the auspices of the National Clean Milk Society. Papers were read dealing with the physical, chemical, bacteriological, and biochemical changes which may occur as a result of pasteurisation, and it may not be out of place in this connexion to refer again to the work of P. Rupp in 1913,¹⁴ which appears to have escaped the notice of many workers in this country. Rupp determined the amount of soluble lime and phosphoric acid in the serum obtained from raw milk and from milk pasteurised at different temperatures, and found that even at 155° F. (68.3° C.), the highest pasteurising temperature used by him, the changes were trifling, within the limits of experimental error. This does not, of course, exclude the possibility that calcium phosphate may be changed from a colloidally dispersed form to a form definitely insoluble, but if calcium phosphate were thus rendered insoluble at pasteurising temperatures we should expect to find a considerable precipitate or sludge left behind at the bottom of the pasteuriser. This is not the case, although it might possibly happen at temperatures nearer the boiling point.

Rupp also investigated the extent to which lactalbumin is coagulated by pasteurisation. He found that no coagulation at all occurs in milk heated to 145° F. (62.8° C.) for 30 minutes. At 150° F. (65.6° C.) the coagulation of albumin had begun, 5.71% being rendered insoluble. At 155° F. (68.3° C.) the quantity had increased to 12.76%, whilst at 160° F. (71.1° C.) 30.87% of the lactalbumin had been coagulated.

The changes in the coagulability of the casein, also, were comparatively slight. In milk pasteurised at temperatures up to 149° F. (65° C.) the casein coagulates with rennin slightly more rapidly than does raw milk. At 158° F. (70° C.) a retardation of rennin coagulation sets in, and at 167° F. (75° C.) the time of coagulation has become nearly double.

¹³ Amer. J. Pharm., 1923, 95, 49.

¹⁴ Bull. 166, Bureau of Animal Industry, U.S. Dept. of Agric., 1913.

The recent introduction in this country of Regulations embodying standards for condensed and dried milks has directed attention to the methods of analysis of these products, and incidentally has revived the controversy as to the adoption of standard methods. While, no doubt, it is highly desirable that analysts should come to some agreement as to which methods are capable of giving the most accurate results, the general trend of opinion seems to be against rigid standardisation, except in special cases. On the one hand, it is contended that manufacturers of, and dealers in, food-stuffs, who buy and sell their products on an analytical basis, are liable constantly to be involved in costly disputes and litigation owing to the varying results obtained by rival analysts employing different methods. On the other hand, it is held that standardisation tends to stereotype methods of analysis, to hamper progress, and to discourage analytical research. Moreover, it is not by any means certain that the adoption of a standard method will invariably secure agreement, and an inaccurate result obtained by careless application of a standard method would be more likely to secure the verdict in a dispute than an accurate result obtained in some other way.

A scheme has been put forward by the Society of Public Analysts, according to which chemists and analysts interested in any particular industries are invited to confer among themselves upon cases where divergent results have occurred owing to the use of different methods of analysis, and to submit reports to appropriate committees of the Society, these reports, after consideration, to be published in *The Analyst*. No specific recommendation will be made as to the employment of any particular methods, the object of the scheme being to insure that all the information available is brought to the notice of Public Analysts and others who may be called upon to undertake the analyses in question.

The analysis of dried milk forms the subject of two papers by H. Jephcott¹⁵ and A. C. Bacharach.¹⁶ They have investigated the degree of accuracy with which lactose can be determined by copper reduction methods, and find that the modified method of F. A. Quisumbing and A. W. Thomas¹⁷ is superior to all others in point of accuracy. The latter authors claimed to have found that in the ordinary method of heating the sugar solution with Fehling's solution in a boiling water bath for 12 minutes considerable errors were introduced by the varying degree of auto-reduction of the Fehling's solution. They also stated that the temperature of the mixture, when immersed in boiling water, was not constant and was subject to variations dependent upon atmospheric pressure.

¹⁵ *Analyst*, 1923, **48**, 529; *Abs.*, 1924, B., 30.

¹⁶ *Ibid.*, 1923, **48**, 521.

¹⁷ *J. Amer. Chem. Soc.*, 1921, **43**, 1503; *J.*, 1921, 899A.

By carrying out the reduction in a thermostat at 80° C., no auto-reduction of Fehling's solution took place, and errors due to variations in temperature were avoided. Many other points were brought out in Quisumbing and Thomas's work, which is worthy of close study by all chemists interested in sugar analysis. It would seem doubtful, however, whether the degree of accuracy claimed by these authors, a percentage error of approximately $\pm 0.12\%$ of copper oxide, is in fact attainable. The writer has found that duplicate experiments, carried out with every precaution, do not always show this high degree of concordance, and Bacharach, working under the exact conditions laid down by Quisumbing and Thomas, obtained consistently a higher weight of copper oxide (about 101.7 instead of 100) for a given weight of lactose. It would seem that sufficient importance has not hitherto been attached to the exact size and shape of the vessel in which the copper reduction is effected. It is quite easy, by altering the size and shape of the vessel and the amount of free air space above the liquid, to obtain results differing from each other by as much as 5%, or even more, of the total weight of copper oxide found.

Although a large number of copper reduction tables are now in existence, adapted to varying methods of working, the only safe course would seem to be for the analyst himself to check his own results on pure sugars under the precise conditions of working adopted by him.

In this connexion an important paper by J. H. Lane and L. Eynon¹⁸ may be noted dealing with the use of methylene blue as an internal indicator in the volumetric determination of sugars. It is stated that by this method results agreeing to within 0.1 c.c. may be obtained in titrations requiring from 15 to 50 c.c. of the sugar solution.

In an American patent¹⁹ a claim is made for the manufacture of a foodstuff by mixing milk with converted starch products and drying the mixture. If such products are placed on sale in this country, the analyst, under the Dried Milk Regulations, may be faced with the problem of determining lactose in presence of maltose, dextrose, and dextrins. This is by no means an easy matter, as is evident from J. L. Baker's work for the Local Government Board in 1914.²⁰

The determination of fat in dried milks by different methods frequently gives rise to discordant results, and H. Jephcott²¹ gives the results of determinations carried out by direct ether extraction, by the Werher-Schmidt method, and by the Röse-Gottlieb method.

¹⁸ *J.*, 1923, 32T.

¹⁹ U.S.P. 1,446,120; *J.*, 1923, 372A.

²⁰ *Food Reports No. 20, Local Government Board*, 1914.

²¹ *Analyst*, 1923, 48, 529; *Abs.*, 1924, B, 30.

His results confirm the experience of most analysts that direct ether extraction is quite useless in the case of dried milks. The percentage of fat obtained, even after extraction for 20 hours, may be more than 5% below the truth. Both the Werner-Schmidt and Röse-Gottlieb methods are capable of yielding correct results, provided that due precautions are taken to avoid loss of fat. Of the two methods, the former is preferable, as it is sometimes difficult to secure complete solution of the milk powder in the Röse-Gottlieb method.

K. Brauer,²² in an examination of the different methods of determining fat in sweetened condensed milks, finds that the most accurate method is that in which proteins and fat are precipitated from the diluted milk by Fehling's copper solution and the dried precipitate is extracted with ether.

A. J. Swaving²³ gives an account of the official control of cheese in Holland in respect of its fat content. The total production of milk in Holland is estimated at 3600 million litres annually, of which only 900 million is consumed as such, the remaining 2700 million litres being turned into butter, cheese, condensed and dried milk, etc. The export of cheese from Holland amounted in 1921 to over 50,000 tons, and it is considered of the highest importance in the interests of the export trade, that there should be an adequate system of official guarantees. Whole milk cheese (Gouda cheese) is required to contain a minimum of 45% of milk fat calculated on the dry cheese. Edam cheese and some brands of Gouda cheese are made from partly skimmed milk, and the lower limit of fat is 40%. In North Holland, where most of this cheese is made, the cheese factories will, apparently, take only one delivery of milk a day, and it is customary for the farmer slightly to skim the afternoon milk, and hold it over until next morning for delivery together with the morning milk. The cheeses are labelled with a transparent disc made of a casein preparation, on which is stamped the minimum fat percentage and the word "volyet" (full cream) for a whole milk cheese. Cheeses made from partly skimmed milk are stamped 40%, 30%, or 20%, and where the fat percentage is below 20% they must be specially marked as made from skim milk. For whole milk cheese the lettering is blue, and for all others black. The constancy of the fat content in whole milk cheeses is remarkable, the actual figures being in most cases between 47 and 51% of fat on the dry product. In 1921 only 0.7% of all the samples examined fell below 45% of fat. A table of figures is given in which the fat content of the original milk varied from 2.55% to 4.01%, the resulting cheeses varying only from 47.9% to 53.3% of fat. The fat content of cheese is, of course, governed primarily by the ratio

²² Z. öffentl. Chem., 1922, 28, 197; J., 1923, 26A.

²³ Z. Unters. Nahr. Genussem., 1923, 45, 6; J., 1923, 621A.

of fat to casein in the original milk, and this is less subject to variation than is the actual fat content of milk. In the United States whole milk cheese is required to contain 50% of fat on the dry solids, but according to Swaving it is impossible for so high a standard to be attained in Holland, although in the greater number of cases the actual figure is approximately 50%.

F. H. van der Laan²⁴ recommends a modified method of determining butter fat in admixture with fats not containing volatile fatty acids. The procedure does not vary in essential details from that usually followed in this country, and moreover the degree of accuracy obtainable does not appear to be greater than can be reached by existing methods.

FRUIT JUICES.

F. Auerbach and D. Krüger²⁵ have published the results of an exhaustive investigation on the determination of malic acid in fruit juices. The determination of the naturally occurring organic acids, malic, citric, lactic, oxalic, succinic, tartaric, etc., in presence of each other is always a matter of some difficulty, and the results obtained by existing processes leave much to be desired in point of accuracy. For the most part they depend on fractional precipitation of the calcium, barium, or lead salts of the acids by alcohol of varying strengths. The precipitates obtained are further examined by ashing them and determining the alkalinity of the ash, by determination of the barium content, or, in the case of the lead salts, by decomposing them with hydrogen sulphide and titrating the free acids. Other methods depend upon the varying resistance to oxidation by permanganate exhibited by the acids. The separation of the acids from each other by these methods is never quite complete, and many contradictory statements appear in the literature as to their relative distribution in various fruits. The question is of some importance in connexion with the analysis of jams and fruit products, since the relative distribution of malic and citric acids may often give valuable information as to the probable constituents of a mixed product.

It has been known for some time that the optical rotation of malic and tartaric acids is enormously increased by the addition of uranium and molybdenum salts, but endeavours to base an analytical method upon this characteristic property have not been successful, owing to the fact that the specific rotations observed vary according to the concentrations of the acids, the amount of molybdenum or uranium in excess, and the reaction of the liquid. By the employment of a large excess of molybdenum or uranium salts and by adjusting the hydrogen ion concentration of the

²⁴ Rec. Trav. Chim., 1922, 41, 724; J., 1923, 287A.

²⁵ Z. Unters. Nahr. Genussern., 1923, 48, 97, 177; Abstr., 1924, B, 32, 111.

solution by means of "buffer" mixtures, Auerbach and Krüger find that they can determine malic acid, in concentration up to 1·5%, in the presence of other acids, with a high degree of accuracy.

The fruit juice is treated with alcohol to precipitate pectic substances, having first been slightly acidified to prevent precipitation of calcium malate by the alcohol. In an aliquot part of the filtrate the malic acid is precipitated, together with other organic acids, as barium salt, by the addition of the correct amount of barium carbonate. The mixed barium precipitate is filtered off and shaken with water, with the addition of solid barium citrate and barium tartrate, until the whole of the barium malate has passed into solution, and the liquid is at the same time saturated with barium citrate and tartrate. The saturation of the solution with these two salts insures that their effect on the rotation, after addition of uranium or molybdenum, is always the same, the only variable being barium malate.

The solution is then divided into three parts. One part is examined direct in the polarimeter, a second part is examined after shaking for four hours with disodium citrate as a "buffer" salt and solid uranium acetate, with subsequent filtration, and a third part after addition of a definite amount of acetic acid and ammonium molybdate. In the case of the uranium compound of lactic acid the solution is levorotatory, while the molybdenum compound is dextrorotatory. The amount of malic acid present is obtained from tables, after applying the necessary corrections for the volume of precipitates, etc. A great advantage is that two separate and independent polarimetric readings are obtained, and the accuracy of the work can be checked by the agreement between the amounts of malic acid found in both cases.

The method is somewhat complicated, but it has evidently been very thoroughly worked out (the account of the work occupies 100 pages) and would appear to give accurate results. The authors find that apple juice contains about 0·6% of malic acid, which represents from 62 to 85% of the total organic acids present. Pear juice contains 0·3% of malic acid, or 66% of the total acids present. Cherry juice contains very nearly as much malic acid as apples. Gooseberry juice contains 0·09% of malic acid, which is only 3 to 4% of the total acid content. Red currants, raspberries, elderberries, bilberries, and tomatoes contain from 0·05% to traces of malic acid, representing not more than 2 to 4% of the total acids present.

These results may be compared with those obtained by C. F. Mutteleit,²⁶ who finds that currant, raspberry, and strawberry juices contain citric acid but no malic acid. He employed the method of fractional precipitation of the barium salts from dilute

²⁶ *Ann. Falsif.*, 1922, 15, 453; *J.*, 1923, 197A.

alcoholic solution. H. Franzen and F. Helwert²⁷ find that apple juice contains chiefly malic acid, together with citric acid and small amounts of succinic and lactic acids, and traces of oxalic acid and unsaturated acids. They separated the acids by fractionating their ethyl esters, converting these into hydrazides and condensing with benzaldehyde.

According to J. M. Weiss, C. R. Downs, and H. P. Corson²⁸ synthetic malic acid is now being produced on a large scale, and it is stated to have a flavour superior to that of citric acid. It is claimed that it may safely be used in place of citric and tartaric acids in food products such as jellies, confectionery, etc., and in beverages.

PRESERVATIVES AND COLOURING MATTERS.

On the vexed question of the use of preservatives and colouring matters in foodstuffs there is little to record, pending the findings of the Departmental Committee which is at present investigating the whole subject. Reference may be made, however, to a useful summary by F. W. Richardson²⁹ of the chief colouring matters used for foodstuffs in the country. Richardson states that Naphthol Yellow S and Tartrazine are the chief yellow food colours now used. Naphthol Yellow, or Martius Yellow, is stated to be poisonous, but the introduction of the sulphonic acid group, forming Naphthol Yellow S, appears to neutralise the toxicity.

Investigators at the U.S. Bureau of Standards have compiled quantitative data on the absorption spectra of the dyestuffs permitted for use in foods.³⁰ Where, as in the United States, the number of permitted dyestuffs is small, the spectroscope affords a most useful means of controlling their presence in foodstuffs. In this country, however, the number of dyes used is much greater, and the absorption spectra of many of the mixtures found in commerce are not sufficiently distinctive, as compared with those of the natural colouring matters, for definite conclusions to be drawn by means of the spectroscope, although it is often useful as a confirmatory test.

P. Buttenberg³¹ draws attention to the substitution in Germany of artificially coloured smoked cod for smoked salmon. Apparently salmon is imported in the salted condition from America, and smoked in Germany after soaking out the excess of salt; but fish of the cod family, appropriately coloured pink with coal-tar dyes, is frequently sold in place of salmon. The method of distinguishing between the two depends on the difference in behaviour

²⁷ *Z. physiol. Chem.*, 1923, 127, 14; *J.*, 1923, 574A.

²⁸ *Ind. Eng. Chem.*, 1923, 15, 628; *J.*, 1923, 1194A.

²⁹ *J. Soc. Dyers and Col.*, 1923, 39, 148.

³⁰ *U.S. Bureau Standards, Sci. Paper* 440, 1922, 121; *J.*, 1923, 9A.

³¹ *Chem.-Zeit.*, 1923, 47, 6; *J.*, 1923 157A.

between the colouring matters when treated with various solvents, and is analogous to the usual methods employed for the detection of artificial colours in other foodstuffs. Probably a more satisfactory differentiation could be obtained by a comparison of the scales, if these are present, as shown by R. E. Essery.³² It would be of interest to ascertain how far the method of protein racemisation, as carried out by H. E. Woodman,³³ would be applicable to the problem of establishing the identity or otherwise of products of this nature.

A. R. Tankard³⁴ has published some interesting statistics on the occurrence of preservatives in foods over a period of ten years. In 7000 samples examined, 9% contained preservatives, and a noteworthy feature is the extraordinary variation in the amount of preservative considered necessary by different manufacturers for the same article. In the case of potted meats and fish preserved with boric acid the ratio of the maximum to the minimum percentage of preservative found is 63 : 1, and in fruit juices containing salicylic acid as much as 84 : 1.

The determination of boric acid in foodstuffs has recently been the subject of discussion, owing to the divergent results frequently obtained in the application of Thomson's well-known method. In this method advantage is taken of the fact that while tricalcium phosphate is insoluble in an alkaline solution, calcium borate is fairly soluble, provided that the degree of alkalinity is not too great. Unless Thomson's directions are closely followed, and the addition of alkali is carried out with the greatest care, low results are obtained, owing to the solution becoming, even locally, too strongly alkaline, with the result that some calcium borate is precipitated together with the phosphate. In the Government Laboratory method³⁵ the precipitation of phosphoric acid as tricalcium phosphate is effected by adding N/10 sodium hydroxide solution drop by drop, with constant shaking, until a faint but permanent pink colour appears, after which the liquid is made up to volume and filtered, prior to titration in presence of glycerol or manitol. An alternative method³⁶ is designed to avoid altogether the risks inherent in precipitation by lime. The greater part of the calcium present is removed in the form of calcium sulphate and the phosphate precipitated by magnesia mixture. After removal of ammonia from the filtrate by boiling with sodium hydroxide, the liquid is neutralised and the titration carried out in the presence of glycerol in the usual manner. There is no doubt that Thomson's method, unless carried out with care, may give results showing a

³² *Analyst*, 1922, 47, 163; *J.*, 1922, 38

³³ *Biochem. J.*, 1921, 15, 187.

³⁴ *Analyst*, 1923, 48, 540.

³⁵ *Ibid.*, 1923, 48, 416; *J.*, 1923, 1241.

³⁶ G. W. Monies-Williams, *ibid.*, 1923, 48, 413; *J.*, 1923, 1242A.

loss of anything up to 50% of the boric acid originally present, a fact which deserves far wider recognition than it appears, so far, to have received.

METALS IN FOODSTUFFS, AND FOOD-POISONING.

K. H. Järvinen³⁷ gives the amounts of metal dissolved from different kinds of cooking vessels by a 40% sugar solution containing 1·5% of citric acid and by a 5% solution of sodium chloride, on boiling for 3 hours. Aluminium vessels dissolved in the citric acid solution to the extent of 120 mg. per kg. of solution, but in the salt solution only 9 mg. was dissolved. Brass was found to give the best results of any of the metals examined. The coating of an enamelled vessel dissolved in the citric acid solution to the extent of as much as 6 g. per kg. of solution. This is in accord with the writer's experience, an enamelled cooking vessel having given up 5·5 g. to one litre of a 1·5% citric acid solution on heating to just below boiling point for 5 hours, although the greater number of enamelled vessels do not give up more than 0·3—0·7 g. per litre under these conditions. Järvinen gives details of a modified "wet ashing" method with nitric and sulphuric acids by which he claims that it is possible to determine in foodstuffs small amounts of all heavy metals, with the exception of mercury.³⁸

W. G. Savage³⁹ has published a valuable book on canned foods, in which the bacteriology of the subject is treated exhaustively. Savage is of opinion that the presence of tin in canned foods is of little significance from the health standpoint, provided it be not excessive, and points out that no cases of poisoning by canned foods have ever been shown to be due to tin. This last statement is no doubt correct, but at the same time it must be borne in mind that injury to health does not necessarily begin only with definite symptoms of poisoning, and in the present state of our knowledge the only safe course is to insist that the tin content of foodstuffs be kept down to the lowest possible limit. This could in many cases be secured by the more extensive adoption of lacquered tins. W. M. Willoughby⁴⁰ is of opinion that it is the presence of salt in canned foods which promotes solution of tin, rather than the action of organic acids.

E. F. Kohman⁴¹ has found that with canned fruit any oxygen left in the tin disappears within a few days when plain tins are used, but that in enamelled tins it disappears much more slowly. This observation is in accord with the suggestion made in last

³⁷ *Z. Unters. Nahr. Genussm.*, 1923, 45, 190; *J.*, 1923, 904A.

³⁸ *Z. Ibid.*, 1923, 45, 183; *J.*, 1923, 903A.

³⁹ "Canned Foods in Relation to Health," by W. G. Savage. Cambridge University Press. 1923.

⁴⁰ *Lancet*, 1923, 204, 255.

⁴¹ *Ind. Eng. Chem.*, 1923, 15, 527; *J.*, 1923, 622A.

year's Annual Report (p. 447) that the solution of tin by canned foods is not due to the direct action of acids on the tin with liberation of hydrogen, but is dependent upon the presence of oxygen, the tin dissolving without the production of gas.

O. Jones⁴² has given a useful summary of the routine factory methods employed in the examination of preserved meats etc.

An unusual case of poisoning due to metallic contamination is reported as having occurred at a large Institution near London.⁴³ Over 200 persons developed typical symptoms of zinc poisoning, which was traced to the consumption of stewed apples prepared in galvanised iron vessels. The stewed fruit on examination was found to contain 7 grains of zinc oxide per pound, and each person probably consumed an equivalent of about 18 to 20 grains of zinc sulphate, the emetic dose of this salt being from 10 to 30 grains.

Perhaps there is no subject in the analytical chemistry of foodstuffs which has received more detailed investigation than the problem of determining minute traces of arsenic. Although the subject was fully ventilated at the time of the Royal Commission on Arsenical Poisoning, in 1903, arsenic still crops up in the most unexpected places, in amounts which must be considered excessive, and its presence can nearly always be traced to the employment of coal or sulphuric acid at some stage in the manufacture or preparation of the foodstuff. In the case of certain samples of cocoa, the presence of arsenic was traced to the use of potassium carbonate of mineral origin, and it is occasionally found in natural foodstuffs and extracts which have never, as far as can be ascertained, been exposed to obvious sources of contamination. A discussion on the determination of arsenic was held in the early part of the year by the Society of Public Analysts in conjunction with the Nottingham Section of the Society of Chemical Industry. Several interesting points were brought out in a paper by J. M. Wilkie,⁴⁴ and the subsequent discussion served a useful purpose in directing the attention of manufacturers and chemists to the need for constant vigilance in the matter of arsenical contamination. An increasing number of chemists are finding that the electrolytic method, using lead electrodes, possesses many advantages over the zinc and acid method, in that, while fully as sensitive, it is easier to control, and is less dependent on the "personal equation."⁴⁵

From time to time one sees reported in the German scientific Press cases of solanine poisoning due to potatoes. One of the earliest recorded cases of this form of poisoning appears to have taken place in 1843, and since then several instances have occurred

⁴² *Analyst*, 1923, **48**, 429.

⁴³ *Lancet*, 1923, **204**, 242.

⁴⁴ *Analyst*, 1923, **48**, 63.

⁴⁵ G. W. Monica Williams, *Analyst*, 1923, **48**, 112, 262.

in France and Germany, mainly among troops. No cases have, to the writer's knowledge, been recorded elsewhere than on the Continent, and so far no explanation based on peculiarities of climate, soil, or methods of cultivation and storage has been advanced to account for the occasional occurrence of a high solanine content. It is not the so-called "industrial" potato which is at fault, but the edible varieties. Normally these contain from 2 to 7 mg. of solanine, or even less, per 100 g., but occasionally the solanine content may rise as high as 40, 50, or even 80 mg. At one time it was thought that only small immature potatoes, and also old ones which had become green from exposure to light, were liable to cause solanine poisoning, but C. Griebel⁴⁶ records two cases arising from the consumption of potatoes in early December, shortly after the crop had been harvested. In every case the skin contained a higher proportion of solanine than the rest of the tuber, and the potatoes in question were characterised by a markedly bitter taste after being cooked. A. Bömer and H. Mattis⁴⁷ also record similar cases where potatoes harvested at the end of October possessed a strongly bitter taste and high solanine content. These authors give analyses of six separate consignments from different parts of Germany during the winter of 1922-23, in which the solanine content ranged from 25.3 up to 58.8 mg. per 100 g., all of which were too bitter for consumption. Samples of these potatoes have been planted on an experimental plot, together with different varieties showing a normal composition, with a view of ascertaining whether soil, climate, or methods of manuring influence the solanine content.

MISCELLANEOUS.

J. Tillmans and A. Güettler⁴⁸ have examined various baking powders from the standpoint of their practical value in bread-making. This depends upon the temperature at which carbon dioxide is evolved and the speed of evolution, and different mixtures are found to vary greatly in this respect. The baking powders were examined by introducing 0.05 g. of the mixture, made up in equivalent proportions, into a carbon dioxide apparatus containing 20 c.c. of saturated sodium chloride solution, and measuring the amount of gas evolved in different times and at different temperatures. Mixtures of sodium bicarbonate with cream of tartar, tartaric acid, potassium bisulphate, or aluminium sulphate, gave off the whole of their carbon dioxide at ordinary temperatures, the proportion evolved in 5 minutes being from 72 to 93%, and the remainder in 15 to 25 minutes. For baking purposes the first named is the best, as approximately 75% of the gas is evolved

⁴⁶ *Z. Unters. Nahr. Genussm.*, 1923, **45**, 175; *J.*, 1923, 303A.

⁴⁷ *Ibid.*, 1923, **45**, 288; *J.*, 1923, 995A.

⁴⁸ *Ibid.*, 1923, **45**, 102; *J.*, 1923, 674A.

in the first 5 minutes, and the whole of the remainder during the subsequent 20 minutes. Mixtures of sodium bicarbonate with tartaric acid, potassium bisulphate, or aluminium sulphate evolve gas too quickly, and favour the formation of large cavities in the bread. Baking powders composed of sodium or ammonium bicarbonates alone or of sodium bicarbonate with primary or secondary calcium phosphate or ammonium chloride, do not give off carbon dioxide until comparatively high temperatures are reached. The most satisfactory of these is the mixture of sodium bicarbonate with primary calcium phosphate, which at 60°C. gives off two-thirds of its carbon dioxide in 25 minutes, although the remaining third is evolved only slowly even at higher temperatures, and the reaction is never complete. The use of a powder which is too slow in action is liable to cause cavities in the loaf, somewhat similar to those formed with a rapidly acting powder. Photographs are given in the paper of typical loaves prepared with different baking powders.

D. W. Stewart⁴⁹ has shown that the cholesterol acetate test is not to be relied on to demonstrate the presence of animal fats in mixtures containing vegetable oils. He separated the sterols from a number of oils by precipitation with digitonin in alcoholic solution, and prepared the crystalline acetates by means of acetic anhydride. Cholesterol acetate from animal fats melted invariably at 114°–114.5° C., except in the case of hardened whale oil, when it melted at a lower temperature. The sterol acetates obtained from vegetable oils showed melting points varying from 125° to 133° C., but with cottonseed oil, repeated recrystallisation brought the melting point down to 114° C. A mixture of 75% of animal fat and 25% of vegetable oil gave a sterol acetate mixture melting, after recrystallisation, at 123° C. It is clear from the above that results obtained in the application of the cholesterol acetate test must be interpreted with caution.

Reference was made in last year's Report to the manufacture of ice for preserving purposes from water containing chlorine or hypochlorites. This idea is apparently being developed, and a patent has now been taken out for charging water with hydrogen peroxide before freezing it.⁵⁰ A solution of hydrogen peroxide is thus formed continuously as the ice melts.

Considerable progress has been made in recent years in the production of dextrose by acid hydrolysis of cellulosic materials. It was shown by R. Willstätter and L. Zephmeister in 1913⁵¹ that cellulose could be hydrolysed completely by treatment at ordinary temperatures with concentrated hydrochloric acid, and solid

⁴⁹ Analyst, 1923, 48, 155; J., 1923, 462A.

⁵⁰ E.P. 201, 772; J., 1923, 996A.

⁵¹ Ber., 1913, 46, 2401. •

dextrose is now being produced in Germany on a technical scale by a similar method, the hydrochloric acid being subsequently recovered by distillation. The sugar thus obtained is contaminated by bitter substances which make it unfit for use except as cattle food. In a recent patent⁵² it is claimed that this may be obviated by treating the cellulosic material before hydrolysis with certain organic solvents which dissolve fats and resins. Several other patents⁵³ have appeared dealing with the production of dextrose from wood or similar material, and there is little doubt that the manufacture will soon be placed on a commercial basis.

⁵² G.P. 362,229; *J.*, 1923, 158A.

⁵³ G.P. 359,866, 362,232, 362,233; *J.*, 1923, 157A. G.P. 362,230; *J.*, 1923, 145A. G.P. 362,231; *J.*, 1923, 158A.

SANITATION AND WATER PURIFICATION.

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In last year's Report Dr. C. L. vert foresaw the possibility of a central department arising in the future to take over the scientific investigation of public health problems. The fulfilment of this forecast appears likely to come about sooner than might have been anticipated. A very large sum of money has been given to this country by the Rockefeller Trustees for the foundation of a School of Hygiene. A committee of selection has appointed Dr. Andrew Balfour as Director of the School. What the School will be is not yet known, but it appears that it will certainly undertake instruction in public health subjects. Research can hardly be separated from such practical subjects, and their embracing character almost necessitates team work on an extensive scale. The gift by the Rockefeller Trustees easily constitutes the most important development in general hygiene in this country during the year. The prospects before the new foundation as an aid to scientific progress are great, and its establishment will be looked forward to with interest.

SEWAGE.

Theory of Purification.

A paper on the theory of sewage purification, entitled "The physical aspect of sewage disposal," has been contributed by F. R. O'Shaughnessy.¹ He states that of the general characteristics commonly found in sewages the most universal and important are the physical properties of the principal constituents—the water and the chief polluting substances. No matter what treatment the sewage may be subjected to, the agents which effect the changes which result in the ultimate destruction of these polluting substances are chiefly biological agents, although the appropriate handling of these agents depends on the incidence of physical laws. The principal solids present are of faecal origin, and because of their physical properties complete separation of solids in general cannot be effected until the colloidal character of the faecal solids has been destroyed. Of the activated sludge process he remarks that the action is biological, the active agents being living things, and that the sludge is non-colloidal, being mostly living material.

¹ J., 1923, 359.

In the discussion on the paper E. Ardern¹ said that the author rightly asked for more clarity of thought in considering the problem of sewage purification, and therefore it was a little disappointing to find that he lacked precision when dealing with the proposals he apparently advocated. It is equally to be regretted that a greater clarity of thought was not manifested in regard to the principles of the purification process. Otherwise it is not conceivable that the ultimate destruction of the polluting substances should be associated with every form of sewage treatment, since it occurs in none, as is evidenced by the large amounts of sludge always remaining; nor that it should be affirmed that the complete separation of the solids from the liquid could not be effected until the colloidal character of the faecal solids had been destroyed, seeing that this character is not destroyed but merely changed, the solids still remaining colloidal; nor, finally, that it should be asserted that the sludge is non-colloidal, being mostly living material, for it consists almost entirely of coagula comprising the colloidal solids of the sewage and also living cells, which are essentially colloidal.³

It is many years since A. S. Jones and W.O. Travis drew attention to the presence and importance of colloids in sewage. They brought forward⁴ a series of experiments which demonstrated that the removal of the colloids and other solids from the sewage constituted the initial purification effect and was the result of physical desolution operations, occurring under sterile as under natural conditions. They adduced a sequence of observations and analytical data in regard to the practical working of contact beds which proved that matters in solution or pseudo-solution which were not calculable as sludge and which could not be deposited by ordinary tank operations yet appeared as solid matter when brought into intimate contact with surfaces. Physical factors exerted a preponderating influence when compared with bacterial factors, as was seen by the rate of deposition being so much in excess of bacterial resolution, the latter not being an immediate operation, but on the contrary an operation completely effected only after the lapse of time. They concluded that sewage was, under all circumstances and at all times, completely clarified by the dissociation from the liquid of its organic and some of its inorganic constituents in a particulate condition, and not, as had been assumed, by the resolution and oxidation of such matters.

These views were the subject of the most strenuous criticism at the time, but they have received subsequently extensive support in the work of other investigators, amongst which may be men-

¹ J., 1923, 3697.

² W. M. Baylies, 2nd Rept. Colloid Chem., 1919, 117.

³ Proc. Inst. Civil. Eng., 1905-6, 164, 68.

tioned that of F. R. O'Shaughnessy⁵ and H. W. Kinnersley,⁶ J. H. Johnston,⁷ G. J. Fowler,⁸ S. E. Melling,⁹ E. Ardern and W. T. Lockett,¹⁰ F. Diénert,¹¹ R. Cambier,¹² H. P. Eddy,¹³ and A. M. Buswell and H. L. Long,¹⁴ and they are now becoming generally accepted.

These principles are applicable also to the activated sludge process, in connexion with which some of the above work was done. A clear demonstration of this has been given by W. O. Travis,¹⁵ who shows that activated sludge differs from the soil and filter bed surfaces merely in the absence of a skeleton framework,¹⁶ and that, like both soil¹⁶ and filtering surfaces, activated sludge is essentially a colloid, and activated sludge absorption simply a manifestation of its colloidal properties. The coagulum which constitutes the beginning and the end of the process is a gel. Each individual gel aggregate has been deposited, either in its original or in its coagulated state, from previous volumes of sewage, and when brought intimately into contact with incoming volumes of sewage assists in coagulating the colloidal solution, in absorbing the soluble and other impurities, and in attracting the organisms contained therein; the degree and rapidity of such physical actions being strictly proportional to the amount of the gel and the condition of its absorbing surface. The activated sludge process, equally with all treatment processes, is primarily and essentially a physical disruption effect, the sewage compound being split up into a coagulum of form-elements with absorbed products and a clear liquid.

This exposition has received valuable confirmation in the remarks of J. A. Reddie¹⁷ in the discussion on O'Shaughnessy's paper, already quoted. He states that whether the method ~~use~~ is the older one of filtration or the more recent one of activated sludge, the primary action—the separation of the colloidal impurity from the liquid—is a physical one. Experiments at the Bradford sewage works with colloidal solutions had shown that the whole of the colloid was removed on passing the solution through a

⁵ J., 1906, 719.

⁶ J. Roy. San. Inst., 1906, 27, 548; Proc. 7th Int. Congr. App. Chem., London, 1909, 8A, 171.

⁷ J., 1911, 1343; J. Inst. San. Eng., 20, 29.

⁸ J., 1914, 1124.

⁹ J., 1915, 937.

¹⁰ Comptes rend., 1917, 165, 1116.

¹¹ Ibid., 1920, 170, 681, 1417.

¹² J. Western Soc. Eng., 28, 259.

¹³ Illinois State Water Survey, Bull. 18, 1923, 82.

¹⁴ Contractors' Report, 1920, 417, 627.

¹⁵ E. J. Russell, 2nd Report Colloid Chem., 1909, 70.

¹⁶ J. M. van Bemmelen, Landw. Versuchs-Stat., 1888, 35, 67.

¹⁷ J., 1923, 3682.

sterile filter of fine grade material. More recent experiments substituting activated sludge for the fine grade material showed that an activated sludge when stirred up in one of the colloid solutions removed the whole of the colloid from the liquid, even when the sludge was previously sterilised by boiling. There appeared to be an adsorption of the colloidal matter present by the filter material and by the sludge particles.

Observations have been made on the nitrogen cycle in the activated sludge process by A. M. Buswell and S. L. Neave.¹⁸ They succeeded in making out a nitrogen balance table for two months' working in winter and for eight months' working from May. During the first period there was a net loss of 0·43%, and during the second period a net gain of 1·8%. They consider that these results are within the limits of experimental error, having regard to the difficulties of average sampling, and afford no foundation for the view that there is a fixation of atmospheric nitrogen during the process.¹⁹ There is, however, a change in the form of the nitrogen during the process, the nitrogen in ammonia, nitrites, and nitrates being converted into protein nitrogen to form the bodies of the organisms present in the sludge.

From a study of the microbiology of activated sludge, A. M. Buswell and H. L. Long²⁰ take the view that purification is accomplished by ingestion by protozoa and by assimilation by bacteria of the organic matter in the sewage and its re-synthesis into the living material of the sludge flocks. In this process the organic matter is changed from colloidal and dissolved states of dispersion to a state in which it settles out.

Practical Studies.

The disposal of sewage is an ever-growing problem. Although the Birmingham, Tame and Rea District Drainage Board already has an area of 52 acres of percolating filters, it is necessary to add an acre of filter bed per annum to keep pace with the increasing volume of sewage. Recently large-scale experiments were completed on the activated sludge process, comparing aeration by blowing with aeration by agitation.²¹ It was found that the sewage was amenable to either the air blowing or the agitation method of treatment, and that a tank liquid forms a better subject for purification than crude sewage, since 60% of its impurity can be removed by an hour's efficient flocculation. It was found also that the flocculated tank liquid could be treated at double the usual rate on a percolating filter.

Upon these findings it has been decided to construct an installa-

¹⁸ Illinois State Water Survey, Bull. 18, 1923, 68.

¹⁹ G. J. Fowler, *J. Indian Inst. Sci.*, 8, 256.

²⁰ Illinois State Water Survey, Bull. 18, 1923, 82.

²¹ J. D. Watson, *Contractors' Record*, 1923, 24, 1930, d1968.

tion embracing adaptations of the usual activated sludge practices. It appears better to leave any description of these proposals until they have been completed and results of their working are available. O'Shaughnessy desires²² that this process should be called the "flocculated sludge" process, which, he says, strictly means "the convenient application of the principles involved at discretion and according to practical requirements," notwithstanding that flocculation is inherent in all purification processes. If a change of name for the activated sludge process is desirable, that suggested by Travis²³—the aerogel process—would appear to be the most suitable, as it embodies the two distinguishing features of the process, the gel—the form in which the deposited colloids exist in activated sludge—and the air, the association of which with the gel is necessary for the maintenance of its activity.

Experiments on the activated sludge process have been conducted by the Illinois State Water Survey for some years. Since the war a new series has been started, and the results have been published by Buswell and his colleagues.²⁴ A Dorr-Peck tank was used, the principal features of which are that during aeration the sewage and sludge circulate in a path leading up from the aeration chamber and returning down a centrally situated cylindrical well, and that the sludge returns automatically from the sedimentation chamber to the aeration chamber. The air used was reduced to the point at which no nitrification took place. This corresponded to 1 cubic foot of air per gallon, which gave a clear and reasonably stable effluent. They deduce from this result that nitrification is not essential to the purification process. The sludge obtained amounted to half a ton per million gallons. Its average moisture was 99.74%, and the content of nitrogen when dried was 5.63%.

Much attention was paid to the difficult problem of drying the sludge. The best results were obtained by the acid-heat-flotation process, in which the activated sludge and dilute sulphuric acid are admitted to the bottom of a tall cylindrical chamber heated by a steam coil to about 50°. Sufficient acid is added to make the reaction of the mixture $p_{H} 4.6$ to $p_{H} 5$. Fine bubbles of carbon dioxide are evolved from the acidified sludge and carry the agglomerated particles to the top of the liquid, where they float as a cake. The moisture in the sludge was reduced from 99% to 93%. The floated sludge drained readily in three days to 85% of moisture, and no odour was developed. Other methods of drying were tried, involving the use of a belt conveyor, a continuous filter, a centrifuge, and a filter-press, but none was satisfactory.

²² *J.*, 1923, 350t.

²³ *Contractors' Record*, 1920, 417.

²⁴ *Illinois State Water Survey, Bull.* 18, 1923.

An extended investigation was made also on the biology of the activated sludge process. As the sludge developed there appeared to be a definite succession of forms appearing. At first there was a predominance of minute ciliates and flagellates, organisms characteristic of sewage. In a few days these diminished until they became negligible in number, and peritrichs, holotrichs, and heterotrichs increased. The peritrichs (especially vorticella) were the predominating organisms, numbering up to 17,000 per c.c. Nematode worms appeared some days after starting and increased to 4000 per c.c., but diminished again. The number of zoological masses at the start was about 100,000 per c.c., and increased after a week to a million, and after two weeks to 2 million, which number remained fairly constant. The zoogloea contained filamentous bacteria, beggiatoa numbering about 5000 per c.c. The conclusion come to is that the sludge particles are not amorphous organic matter, but are composed of a synthetic gelatinous matrix in which filamentous and unicellular bacteria are imbedded, and on which various protozoa crawl and feed.

At the New Jersey Experiment Station observations have been made²⁵ on the biology of percolating filters. The slimy film on the surface contains algae and in the interior fungi. The film contains protozoa, in number up to 300,000 per c.c., and nematode worms up to 100,000 per c.c. A sloughing of the film was observed to take place in spring and autumn.

The name of the Corporation of Glasgow must be added to the list of those Local Authorities in this country who have investigated the activated sludge process. In a report by the Corporation Chemist²⁶ an account is given of a large-scale experimental plant treating 200,000 gallons a day on the continuous flow system. In this installation, following the example of Sheffield, it was decided to use mechanical agitation instead of compressed air as the method of aeration. The tank, of 80,000 gals. capacity, was divided so as to make a continuous channel 640 ft. long and 5 ft. deep. Aeration was effected by four paddle wheels revolving on a shaft across the centre of the tank. The rate of surface circulation in the tank was 1.25 ft. per sec. The plant was worked for nearly two years. Although fluctuations in the strength of the sewage and variations in the character and proportion of trade waste present were frequent, the effluent was always well purified and stable. The analysis of the effluent during the last month of working showed free ammonia 0.03 grain per gal., albuminoid 0.068, oxidised nitrogen 0.87, chlorine 4.55, and oxygen absorbed in four hours 1.693. The absorption of dissolved oxygen varied from

²⁵ W. Rudolfs, Eng. News Rec., 1923, 18, 719.

²⁶ F. W. Harris, Report on the activated sludge process of sewage purification, 1923; J., 1923, 945A.

1.23 parts to 0.26 part per 100,000, with an average over the whole period of 0.56 part. Aeration by mechanical agitation was successful, therefore, in a tank of the length and depth given, but this was about the limit of its capability, for attempts to increase the volume of sewage to a quarter of a million gallons daily soon caused the effluent to deteriorate.

The degree of aeration of the sewage in the agitation tank is of importance. It was determined by aerating fresh sewage in the tank for 6 hours and determining the dissolved oxygen every half-hour. This gave the maximum aeration under the conditions. It was found that the dissolved oxygen began to increase at once after aeration started, and rose quickly at first and then slowly until an amount of 5.6 c.c. per litre was obtained at the close of the aeration period. This result corresponded to 76% of saturation. The half-hourly sampling was continued daily, and the average results for the first month, when the volume of sludge present was 18.5%, showed no increase in dissolved oxygen for the first half-hour, followed by a rise, slower than in the fresh sewage, to an amount of 3.9 c.c. per litre. For the next two months, when the volume of sludge was 34% and 36%, there was very little or no dissolved oxygen in the first hour and a half, and then a gradual rise to 3 c.c. and 2.5 c.c. per litre. These results show that the consumption of oxygen by the sludge during the early period of aeration was more than the sewage could take up during that time, and that at the end of the period the aeration had not reached the maximum.

The amount of oxygen required by the activated sludge in an aeration tank is difficult to determine accurately, but Harris made an attempt to do so. The dissolved oxygen was determined in a sample of the tank contents; a duplicate sample was agitated in a completely filled bottle for half an hour, and then the dissolved oxygen determined. The difference between these two results gave the dissolved oxygen used by the sludge present in half an hour. This difference gave amounts varying between 21.7 and 38.6 cub. ft., calculated on the whole contents of the tank. The corresponding figures per gallon of sewage treated were 0.0052 and 0.0092 cub. ft. The consumption in a continuous flow tank would be greater than in a closed bottle, and allowing for this as far as possible, the amount of oxygen required by the biological process in the aeration tank was considered to be 0.0083-0.0124 cub. ft. of oxygen per gallon of sewage treated, corresponding to 0.04-0.059 cub. ft. of air.

The amount of oxygen required by sewage, as distinct from activated sludge, has been investigated by C. L. Peck,²⁷ who finds that where raw sewage is aerated its oxygen demand is satisfied at

an extremely rapid rate for half an hour or so, after which the rate is slow, and that during the early period the rate is not affected by the presence of activated sludge. He considers that treatment should consist in sedimentation²⁶ to remove the suspended organic solids, aeration alone to oxidise the readily oxidisable matter and to expel the gases of decomposition, and aeration in presence of activated sludge to oxidise colloidal substances. During aeration, the air must be supplied in sufficient amount to maintain aerobic conditions and to keep the sludge in suspension. The former is best effected by aeration from the bottom of the sewage, while for the latter mechanical agitation should be employed as it is cheaper.

Activated sludge cannot be de-watered readily, and not by pressure alone, which has always been a drawback to the adoption of the process on a large scale. Recently the acidification of the sludge has given promise of some success. Peck finds that when concentrated sulphuric acid is added to the sludge without agitation, and the mixture is heated to 30°, all the sludge rises to the surface and can be drawn off and drained. The amount of water in the floated sludge is 89%, compared with 99% in the original; after draining for a day it is 77%; after two days 66%; three days 59%; and three weeks 26%. These experiments have been developed into the acid-heat-flotation process, previously referred to as employed by the Illinois State Water Survey.

Another acid process which has been applied also to ordinary sludge is the Maclachlan process,²⁸ in which hot sulphur dioxide is blown into the sludge until a hydrogen ion concentration corresponding to p_{H} 3.8 is attained, when the solids coagulate. The sludge is then passed through a drum screen, where the sheet of solids obtained contains 80% of moisture, and may be air-dried without nuisance.

A new sewerage and sewage disposal scheme is in course of construction for the town of Prestatyn, on the North Wales coast. The sewage will be dealt with by storing it in large tanks at the disposal site on the eastern boundary of the district. From the gravitation sewer and rising main the crude sewage discharges into a receiving chamber forming part of the storage tanks. The untreated sewage will be discharged from these tanks one hour after the commencement of ebb tide, the outlet remaining open for discharge for four hours. The discharge pipe runs in the foreshore to low-water mark of ordinary spring tide.²⁹ This is the scheme for a watering-place and holiday resort with a population of 9000 in the summer months. Even at the present day every new sewage scheme does not indicate progress in sanitation.

²⁶ Peck, *loc. cit.*

²⁸ J. H. Blizzard, *Contractors' Record*, 1923, 24, 2063.

WATER.

It has long been considered that there was a connexion between simple goitre or "Derbyshire neck" and water supply. The disease is endemic in several districts, and it has been observed that 7% of the children may develop it. The cause is not known with certainty. The disease has been attributed to the presence of a bacterium in the water, to excess of iron and calcium salts, and to the absence of iodides from the water. The enlargement of the thyroid gland in individual cases is attributed to a greater physiological demand upon the functions of the gland than it can cope with normally. The gland therefore enlarges in an endeavour to supply the deficiency. The characteristic constituent of the gland is iodine in the form of thyroxin. One method of medical treatment has been the administration of the dried gland or of iodides, which has been found beneficial. Recently³⁰ public health authorities in the United States and Switzerland have adopted the view that the disease is caused by a deficiency of iodine in the local water supply, and that it would be desirable as a measure of preventive medicine to make good this deficiency. At Rochester, N.Y., these preventive measures were started in the spring by the addition of sodium iodide to the water reservoir supplying the town. The quantity added was 16 lb. a day for two weeks. This amount was equivalent to a five-thousandth of a gram of iodine to a gallon of water, and was twenty times greater than the amount naturally present. The treatment was to be repeated again in the autumn. The cost is estimated at 2000 dollars a year. It is considered that this very small addition of iodine twice a year will be sufficient to prevent the development of goitre in persons drinking the water. If the treatment is successful, it may help to settle the question of the cause of the disease. This is an unusual case of the treatment of a water supply for the benefit of the few and not of the many. It will be interesting to observe whether the drinking of the treated water has any effect upon normal individuals in the town.

Although in the States this open announcement of the chemical treatment of a water supply appears to be received without demur, it is doubtful whether the same reception would be accorded to a similar proposal in this country. It is fortunate, therefore, that the necessity for the present chemical treatment of the London water supply arose during the war, when it could be introduced without the fact being announced in the daily press. Even now very few consumers realise that they are drinking chemically treated water. The history of the chlorination of Thames water, in the enthusiastic words of A. C. Houston, its author, "reads

³⁰ B. C. Little, *J. Amer. Water Works Assoc.*, 1923, 10, 556; *J.*, 1923, 945A.

almost like a romance. Born and bred of the war, it is still in active operation, and, so long as the cost of chlorine for sterilisation falls far short of the cost of coal for pumping, is likely to be continued indefinitely.³¹ This year the saving effected amounted to £16,000.

About 70–80 million gallons daily of raw Thames water is taken from the river at Bell Weir, and as it enters the Staines Aqueduct it is chlorinated to the extent of 0·5 part per million. The chlorinated water takes three hours to pass down the Aqueduct to the sand filters lower down the river. Although the water is filtered so soon as three hours after treatment, no taste troubles have arisen, or perhaps it would be more correct to say that no complaints as to taste have reached the Water Board. When the Thames is in high flood the treatment is discontinued, and Staines reservoir water, which has been stored for a very long time, is used instead. The effect of chlorination is to improve the water bacteriologically about a thousand times.

The New River, on the other hand, is sufficiently pure not to require sterilisation before filtration, except during the winter months. In this case, however, grave difficulties have arisen by the appearance of taste in the treated water. The taste-imparting substances appear to be absorbed by the filter beds and to be stored up for a period, after which they are allowed to escape, and continue to do so until all the taste substance has been yielded up by the filter. This unfortunate factor has been overcome by skilful dosage and the supplemental use of permanganate as a taste remover.

In the New River also abundant growths of diatoms develop in the spring. Experiments have shown that rapid filtration removes these most successfully. A practical installation for this purpose is being erected.

In addition to its well known use as a source of drinking water, the Thames is used as a source of industrial water. A very important instance of the purification of the river water, in this case the water from the tidal portion of the river off Beckton, for this purpose has been put into service this year by the Gas Light and Coke Company, Ltd. The scheme deals with four million gallons a day³² in a rapid filtration plant of duplicate units, consisting of a settling basin and four filters each.

The water pumped from the river is delivered into a concrete chamber with baffles, whence it passes into a measuring channel and flows over two rectangular brass weirs, one larger than the other. The exact quantity of water passing over the larger weir is measured and recorded on an integrating rheograph. A definite portion of

³¹ *J. Roy. San. Inst.*, 1923, 44, 63.

³² United Water Softeners, Limited, *Engineer*, 1923, 136, 168.

the water passes by means of the smaller weir into an automatic measuring apparatus, fitted with a chemical container and a chemical mixing valve so adjusted as to deliver the exact quantity of lime necessary to coagulate and precipitate the suspended and hardening substances contained in Thames water at Beckton. The lime solution is prepared in two mixing tanks, furnished with agitators, and the solution passes by pipes to the chemical container.

The water with the added lime solution falls into a long trough and then passes into distributing channels communicating with the settling basins. These are constructed of concrete with sloping bottoms and hold 600,000 gallons, thus allowing nearly four hours for reaction and sedimentation when the plant is working at full capacity. For clearing out the basins, sluice valves and drains are provided, but thorough cleaning is required only about every ten weeks. The water enters the settling basins under baffles and overflows the sill into a trough leading to the filters. During passage through the basins the heavier impurities and a considerable portion of the coagulated matter are precipitated.

A system of communicating troughs stands over the filters from which the water overflows on to the whole superficial area of the filters. The total area is 2112 square feet, each foot filtering nearly 80 gallons per hour. The filtering medium is sifted and graded quartz sand supported on a bed of washed and graded gravel. Below the gravel is a system of collecting tubes furnished with safety strainers, by which the water is drawn off from all parts of the filter at the same time. The water thus collected is discharged through a central pipe and passes through a ball control valve to the automatic rate-of-flow controller. The ball valve operates the filter outlet and ensures that water is always retained in the filter bed to a certain level; also it retards the outflow after cleaning, so that time for the formation of the surface film is given before the full discharge takes place. The rate-of-flow controller is situated in an outer inspection chamber, and consists essentially of a floating piston attached to a moving throttle diaphragm, which opens and closes the outlet of the valve in accordance with the change of head in the filters. From the inspection chamber, where the appearance of the filtered water can be noted, the water passes over a weir into the filtered water channel to a reservoir with a capacity of 60,000 gallons.

A tower is provided with a capacity of 40,000 gallons in which filtered water is stored for cleaning the beds. The cleansing operation is performed by agitating the filtering medium with compressed air at a pressure of 3-5 lb. per sq. in. for about two minutes. A reverse current of water is then supplied to the underside of the filter bed, and in its passage upward through the bed the impurities deposited on the sand are floated off into connecting

waste troughs and pass into a drain. The cleansing process takes about ten minutes.

The filtered water is used throughout the works for all purposes, excepting steam-raising.

In the States the subject of taste and odour after chlorination has been studied by F. H. Waring.³³ There the towns of Cincinnati, Columbus, and Toledo receive river waters which have been treated with a clarifying agent, such as ferrous sulphate and lime, or aluminium sulphate, rapidly filtered and then sterilised with chlorine. At any time when the rivers are in flood it has been noticed that an "earthy" odour and taste develop in the chlorinated water, or if the river has been low and frozen over that a "grassy" odour develops. These odours subside when the rivers begin to return to normal conditions. Chemical deterioration of the water accompanies the periods of taste; the oxygen absorption increases and the dissolved oxygen decreases. It is evident that the usual oxidative changes are occurring in presence of insufficient dissolved oxygen, and to these partially anaerobic conditions is ascribed the production of taste and odour. It was found that the matter could be remedied by slightly increasing the amount of coagulant used, an excess of 2-3 grains of aluminium sulphate per gallon being sufficient. It is considered that the remedy would be facilitated by aeration of the water.

The effect of slight acidity in rendering water safe to drink has long been recognised by the use of tablets of acid potassium or sodium sulphate. This arises from the fact that many bacteria are very sensitive to the reaction of the culture medium, and therefore to the reaction of any natural water in which they might be present. This point has been investigated at the Marine Biological Laboratory at Plymouth,³⁴ and W. R. G. Atkins states that water-borne bacteria might be killed by altering the hydrogen ion concentration of the water, using, however, alkalis rather than acids as being more convenient to handle. Town supplies are normally between p_{H} 6.8 and p_{H} 8, which range is favourable to the survival of the typhoid and cholera groups of organisms. By addition of potassium or sodium carbonate the hydrogen ion concentration could be altered to p_{H} 10.5, which would suffice to kill the organisms mentioned. This might be done very conveniently in the case of local water supplies by the addition of wood ashes, only a small quantity being required.

DISINFECTANTS.

In testing the germicidal power of a disinfectant it is convenient to compare its action with that of a pure chemical substance, for

³³ *J. Amer. Water Works Assoc.*, 1923, 10, 75; *J.*, 1923, 419A.

³⁴ *J. State Med.*, 1923, 31, 223.

which purpose phenol is nearly always used. The specimen of crystals used is examined for purity by the bromine titration method.

J. T. A. Walker and J. M. Weiss³⁵ point out that this method does not indicate the presence of small amounts of cresol in phenol, the cresol being returned as phenol. This failure to indicate the presence of cresol might lead to grave errors in practice, as cresol is three times as strong a germicide as phenol. They synthesised phenol from pure benzene, and found that the solidifying point of the melted crystals was 40·5°. This was in agreement with Eger's result of 40·9° for the pure substance.³⁶

Commercial samples of pure phenol after drying had solidifying points of 34·4°, 38°, 38·8°, and 39·9°. The corresponding amounts of cresol, by calculation, to these figures were 12, 4·8, 3·4, and 1·1%, which agreed closely with the results of analyses. These amounts of impurity would be likely to cause differences in results in practice, according to the sample used as standard. A very interesting experiment on this point was made, the carbolic acid coefficient of the same disinfectant being determined by the Rideal-Walker method with each sample of phenol in succession. The coefficients obtained were 16, 18·5, 19, and 20, and 20 also with the pure synthetic phenol. The possibility of such differences would be of importance in a strict comparison of the germicidal powers of different disinfectants carried out in different laboratories, and especially in testing disinfectants supplied under contract.

The authors recommend that the purity of a specimen of phenol to be used as a standard should be determined by the solidifying point method, and that no phenol with a solidifying point below 40° should be considered pure.

³⁵ *Medical Officer*, 1923, **29**, 226.

³⁶ *Pharm. Zeit.*, 1903, 210.

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS

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ANIMAL AND BACTERIAL PRODUCTS.

DURING the past year two important communications have appeared by H. W. Dudley¹ and by J. J. Abel, C. A. Rouiller, and E. M. K. Geiling,² dealing with the pituitary hormones. The former worker found that a crystalline picrate could be isolated from the butyl alcohol extract of the aqueous digest of the glands possessing the characteristic action of pituitary on plain muscle (oxytocic effect) and on the blood pressure, and in its activity equalling histamine. This picrate was identified as potassium creatinine picrate contaminated by a trace of active material. By crystallisation from alcohol the active substances remained behind in the solvent and were divisible into an acetone-soluble, R, and an acetone insoluble, A, fraction. A was twelve times as active as histamine on the guinea-pig's uterus (oxytocic effect) and tested on the blood pressure showed a strong pressor effect but was free from depressor constituents, whereas R had one-twentieth the oxytocic activity of A and produced a strong depressor action followed by a moderate pressor action. This and other evidence supports the earlier conclusions of Dale and Dudley that there are at least two principles if not three. These results may be contrasted with those of Abel and his co-workers, who use new adsorption methods for purifying the active principle. Their purest preparation, which was matched against histamine phosphate, had an oxytocic activity 1000 to 1250 times as powerful. A dose of 0.01 mg. raises the blood pressure of a cat and 0.05 mg. produces a marked diuresis in rabbits. No methods have hitherto been successful in the hands of the authors for the division of the product into fractions with different physiological activities as found by Dudley. The product is still a varnish, but its aqueous and alcoholic solutions no longer produce precipitates with picric or picrolonic acids, mercuric

¹ *J. Pharm. Exp. Ther.*, 1923, 21, 403; *J. Chem. Soc.*, 1923, 124, i, 629.

² *J. Amer. Med. Assoc.*, 1923, 80, 1875; *Rep. Internat. Physiol. Cong.*, Edin., 1923; *J. Pharm. Exp. Ther.*, 1923, 22, 289.

chloride, or tannin, and phosphotungstic acid only precipitates it incompletely. The novel methods adopted for its purification have recently been published in detail and are thought suitable for the isolation of secretin and insulin.

Some years ago Richet isolated two crude poisons, thalassin and congestin, from the sea-anemone. A pure crystalline toxic constituent has now been isolated by D. Ackermann, F. Holtz, and H. Reinwein.³ From 33 kg. of sea-anemone (*Aktinia equina*) they obtained 12 grams of tetramethylammonium chloride, a new constituent of the plant or animal kingdom, characterised by its intense curare action on the frog, 0.01 mg. producing complete paralysis in 3 minutes.

The naturally occurring amino-acids are valuable experimental materials, and their availability at a reasonable price is much to be desired. A useful process for isolating arginine,



has been described by A. Kossel and R. E. Gross⁴ by means of a specific precipitant in the 7-sulphonic acid of Martius Yellow (2,4-dinitro-1-naphthol-7-sulphonic acid). Protein hydrolysates freed from excess of acid give a precipitate of the arginine salt of this sulphonie acid, which salt has a solubility in water of less than 0.2%.

The modern science of bacteriology is one of wonderful technique, so that delicate phenomena covered by such terms as agglutination, complement fixation, precipitin formation, of which the chemical basis and mechanism are almost unknown, are reproducible with precision. Some interesting and probably significant observations are recorded by M. Heidelberger and D. T. Avery,⁵ who have made an attempt to isolate the substance from the cultural fluid in which pneumococci are grown *in vitro* which precipitates specifically in anti-pneumococcus serum. By fractional precipitation of 75 litres of broth in which pneumococcus had been grown, by alcohol or acetone and finally ammonium sulphate, one gram of a varnish has been obtained containing 1.2% of nitrogen. It was essentially a polysaccharide, giving 79% of reducing sugars on hydrolysis and yielding glucosazone. It gave a reaction with immune sera at a dilution of one in three million. This suggests an unsuspected specificity relationship between carbohydrates and bacteria. It is, however, possible that the specific substance is nitrogenous and only associated with the carbohydrate.

To a similar category belong some equally surprising results of W. A. Perlzweig and G. I. Steffen.⁶ In 1902 Pick isolated from

³ Z. Biol., 1923, 79, 113; J., 1923, 1245.

⁴ J., 1928, 147A.

⁵ J. Expt. Med., 1923, 38, 73.

⁶ Ibid., 1923, 38, 181.

young typhoid bacilli "coagulin B" which gave a precipitate with immune sera, was protein-free, soluble in alcohol, and resistant to heat and proteolytic enzymes. It would not, however, act as an immunising antigen. The two authors mentioned, working with pneumococcus, have isolated an immunising antigen by tryptic digestion and extraction of the digest with 70-90% alcohol. It is thermo-stable, non-lipoidal, and non-toxic and contains only a trace of nitrogen. It appears to be very much simpler than native bacterial protein. It will be observed that three independent groups of workers studying the chemistry of different phenomena of great importance in serum therapy arrive at results which suggest that non-nitrogenous materials, associated with bacteria, play a significant rôle in their reactions.

Insulin.—Although insulin has proved wonderfully successful in diabetic therapy, little is known as to the mechanism of its action or as to its chemical constitution. A summary of the methods, which have by no means reached finality, used for its isolation has been given by C. H. Best and D. A. Scott.⁷ The pancreatic glands are extracted with 95% denatured alcohol acidified with acetic acid. Aqueous extractions have been tried but the product is much less easily purified. The methods used for purification are five in number, (1) precipitation by half saturation with ammonium sulphate,⁸ (2) precipitation by adjusting the hydrogen ion concentration⁹ of the medium to the isoelectric point, about $p_{H} 5$, (3) adsorption by benzoic acid from aqueous solution,¹⁰ (4) adsorption by charcoal,⁹ (5) precipitation by picric acid.¹⁰ The last-mentioned method has the advantage that the insulin can be obtained as a stable powder by conversion of the picrate into the hydrochloride by means of alcoholic hydrochloric acid and ether. Such a product was found by Dudley to be free from phosphate and organically combined phosphorus, to give Molisch's reaction for carbohydrate, the biuret, Pauly, and organic sulphur reactions. It was fairly stable to acids but much less to alkali, and was destroyed by pepsin and by trypsin. It was also non-dialysable. Its complexity is evidently greater than was at first thought to be the case, being of quite a different order from the pituitary and suprarenal principles.

J. B. Collip, who contributed to the large-scale development of the isolation of insulin,¹¹ has turned his attention to the occurrence of insulin-like substances where glycogen is present in nature and has isolated from yeast,¹² wheat leaves, onions, lettuce, barley

⁷ *J. Biol. Chem.*, 1923, **57**, 709; *Abs.*, 1924, B, 112.

⁸ E. A. Doisy, M. Somogyi, and P. A. Shaffer, *ibid.*, 1923, **55**, 31.

⁹ P. J. Moloney and D. M. Findlay, *ibid.*, 1923, **57**, 359, 709.

¹⁰ H. W. Dudley, *Biochem. J.*, 1923, **17**, 376; *J.*, 1923, **1245A**.

¹¹ *Chem. Abst.*, 1922, **16**, 3115.

¹² *Nature*, 1923, **111**, 571; *J. Chem. Soc.*, 1923, i, 728.

root, and clam tissue,¹³ a crude product which has the action of insulin but in which the effect develops much more slowly. The principle in plants is called glucokinin. A similar preparation has also been made from yeast by H. B. Hutchinson, W. Smith, and L. B. Winter.¹⁴ It is too early to state whether this product from these sources will have any commercial application.

GLUCOSIDES.

The assay of digitalis is usually effected by a biological method, although chemical methods have been proposed. Martindale¹⁵ proposed a colorimetric method depending on the reaction with Frohde's reagent (ammonium molybdate in sulphuric acid). A new method has recently been evolved by A. Knudson and M. Dresbach, depending on an observation of Baljet, in 1918,¹⁶ who showed that digitalis glucosides gave an orange-red colour with alkaline picrate solutions. These authors have applied it to the quantitative assay of a number of digitalis tinctures, fluid extracts, and infusions and find a close correspondence with the biological method.¹⁵ Still more recently they have extended it to strophanthus. In either case, the tincture, for instance, is decolorised by lead acetate, the lead removed as phosphate, and the liquid treated with an alkaline picrate. The maximum colour develops in 20 minutes and is compared with a standard such as ouabain or bichromate. In both cases the chemical assay is claimed to give an estimate of potential cardiac activity.¹⁶

The inter-relation of the animal and vegetable heart poisons, the phytosterols, and terpenes has been emphasised in previous Reports.¹⁷ A recent paper by A. Windaus and G. Brandstetter outlines a research in this group which is likely to have far-reaching consequences.¹⁸ In a former paper Windaus and Hermanns¹⁹ pointed out that the sugar-free products of the heart poisons are hydroxy lactones and have probably a similar carbon skeleton loaded differently with oxygen. Thus antiarigenin is $C_{21}H_{28}O_5$, digitoxigenin $C_{22}H_{32}O_4$, digitaligenin $C_{24}H_{32}O_3$, strophanthidin (cymarigenin) $C_{22}H_{30}O_5$, or according to Jacobs and Heidelberger²⁰ $C_{21}H_{32}O_6$, and bufotalin $C_{24}H_{30}O_3$. *Digitilatum verum* has now been prepared pure in a yield of 22 g. from 17 kg. of *digitalis* seeds, and melts at 211°–212°. By catalytic reduction with palladium and hydrogen, the genin, digitaligenin, absorbs six atoms of hydrogen, forming hexahydrodigitaligenin, $C_{24}H_{38}O_3$. As its three oxygen atoms are

¹³ *J. Biol. Chem.*, 1923, **56**, 543; *J.*, 1923, 856A.

¹⁴ *Nature*, 1923, **112**, 205; *Biochem. J.*, 1923, **17**, 683.

¹⁵ *J. Pharm. Exp. Ther.*, 1922, **20**, 205.

¹⁶ *Rep. Internat. Physiol. Cong.*, Edin., 1923.

¹⁷ *Ann. Repts.*, 1922, **7**, 495.

¹⁸ *Ber.*, 1923, **36**, 2001; *J.*, 1923, 1150A.

¹⁹ *Ber.*, 1915, **48**, 979; *J.*, 1915, 851.

²⁰ *J. Biol. Chem.*, 1922, **44**, 253.

present as a lactone and a hydroxyl group it possesses 8 atoms of hydrogen less than a saturated lactone of the paraffin series with C₂₄. It contains therefore four rings, as do cholesterol, the bile acids, and bufotalan, the reduction product of bufotalein, with which it is isomeric. It differs from bufotalan in that its OH group is secondary, yielding, a ketone on oxidation and a lactone C₂₄H₃₈O₂ on reduction of the ketone by Clemmensen's method. This substance without the OH group no longer gives the well-known colour reaction with acetic anhydride and sulphuric acid.

The authors propose to examine in a similar way periplocin, ouabain, digitoxin, antiarin, and scillaren to see what is the inter-relation of the saturated reduction products.

ESSENTIAL OILS.

At the present time thymol is the focus of attention and widespread interest. As an antiseptic it is a product of considerable commercial importance, and it is either being made or processes are being worked out for its preparation by at least four or five methods. In addition, it can serve as the basis for the preparation of menthol, the optically active variety of which is practically a Japanese monopoly. Before the war thymol was sold at 7s. per lb., in January of this year it was quoted at 17s. 6d. per lb., and in November at 13s. 6d. per lb. The chief natural source of thymol is ajowan seed grown in India, whence the whole crop was formerly exported to Germany. In the last few years it has been manufactured in Central India on an extensive scale, and 10,500 lb. of thymol was exported²¹ from India in the two years ending June, 1919. France has no natural supply of thymol, and suggestions have been made that *Ocimum gratissimum*, which grows on the Ivory Coast, should be cultivated.²² The oil gives 44% of phenols, chiefly thymol.

Synthetic thymol is, however, likely to be a serious competitor of natural thymol. It is now being manufactured in Australia from piperitone by an oxidation process in 90% yield.²³ Piperitone or peppermint ketone, offered to British manufacturers at 4s. 6d. per lb., is obtained from the Eucalypts, trees indigenous to Australia but not at present cultivated. It is stated that Germany is prepared to take the whole of the eucalyptus oils that Australia can produce.

Another potential source is cymene, the by-product in the sulphite-cellulose industry, of which two million gallons is wasted annually in Canada and the United States. The Phillips patent, dedicated to the people of the United States, points out that thymol costs 4·5 dollars per lb. and claims that the synthetic could

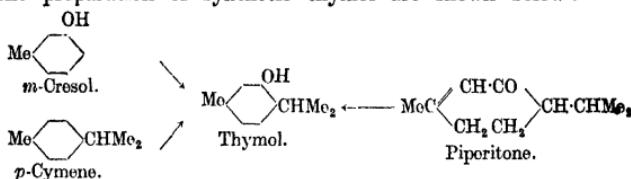
²¹ *Perf. Essent. Oil Rec.*, 1920, 11, 297.

²² *Ibid.*, 1923, 14, 154.

²³ *Ibid.*, 1923, 14, 256.

be made for 2·5 dollars per lb.²⁴ * Several chemical manufacturers have become interested in this patent, which is an improvement on previous processes.²⁵ Cymene is nitrated, the product reduced to cymidine, which is sulphonated and a new method used for eliminating the amino-group by conversion primarily into cymyl-hydrazinesulphonic acid. The hydrazine group is removed and the sulphonic acid finally fused with potash.²⁶ Another allied process has also been patented by R. H. McKee,²⁷ who sulphonates spruce turpentine with fuming sulphuric acid with production of mixed sulphonic acids, which on fusion with caustic soda yield thymol and carvacrol.

In England and in Germany many patents²⁸ have been taken out by two firms for the preparation of thymol by condensation of sulphonated *m*-cresol with isopropyl alcohol, the sulphonic acid groups being removed by steam. The process is based on a discovery of Mazzara,²⁹ who used anhydrous magnesium chloride as condensing agent. An improved process has recently been patented by Howards and Sons and J. W. Blagden,³⁰ in which sulphonation is avoided by use of phosphoric acid. The starting materials for the preparation of synthetic thymol are shown below:—



Closely linked with the chemistry of thymol and pipеритоне is that of the menthones and menthols. The subject is more involved than a perusal of the patents would indicate, owing to the fact that menthone exists in two forms, menthone and isomenthone, the former of which on reduction gives rise to menthol and neomenthol and the latter to isomenthol and neoisomenthol.³¹ Each of these can occur in optically active modifications. H. G. Smith and A. R. Penfold³² claimed that piperitone on reduction with hydrogen and nickel at 175°–180° gave an almost quantitative yield of menthone, and this on reduction with sodium and moist ether gave menthol.

²⁴ *Ibid.*, 1923, 14, 26.

²⁵ *Ann. Repts.*, 1919, 4, 497.

²⁶ M. Phillips, *J. Amer. Chem. Soc.*, 1923, 45, 1489; *J.*, 1923, 742A.

²⁷ U.S.P. 1,449,121; *J.*, 1923, 521A.

²⁸ Badische Aminil u. Soda Fabrik, E.P. 186,202, *J.*, 1923, 879A. Howards and Sons and J. W. Blagden, E.P. 197,848; *J.*, 1923, 743A.

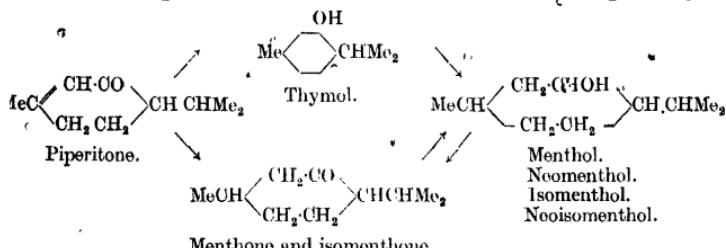
²⁹ *Gazz. Chim.*, 1882, 12, 505.

³⁰ E.P. 200,151; *J.*, 1923, 950A.

³¹ R. H. Burkard and W. O. Littlebury, *J. Chem. Soc.*, 1912, 101, 109; *J.*, 1912, 457.

³² *Proc. Roy. Soc. N.S.W.*, 1920, 54, 40; *J.*, 1922, 78A.

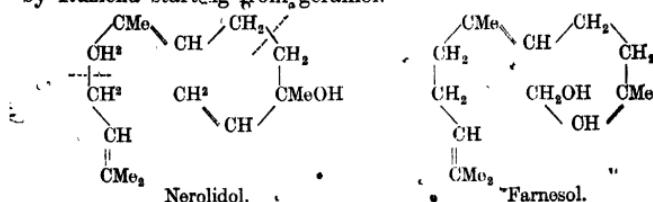
This does not, however, agree with the recently published observations of R. S. Hughesdon, H. G. Smith, and J. Read,³³ who reduced *dl*-, *d*-, and *l*-piperitones in presence of palladium at 25° or nickel at 180° with production of *dl*-, *d*-, and *l*-isomenthones respectively.



Again these latter workers find a bimolecular ketone as the main product of the electrolytic reduction, whereas Penfold and F. R. Morrison³⁴ obtained a quantitative yield of isomenthone.

The Rheinische Kampfer Fabrik³⁵ have patented the reduction of thymol to the menthols by heating with hydrogen under pressure in the presence of nickel, cobalt, platinum, or palladium. The product is a solid inactive menthol (or menthols) and a liquid, which latter can be dehydrogenised by copper or nickel oxide to the menthones and the latter re-hydrogenised with production of more solid menthol. British firms have put on the market³⁶ an optically inactive solid synthetic menthol, m.p. 28°–30° (natural *l*-menthol 45°) and a liquid synthetic menthol. Both of these are probably mixtures. The production of *l*-menthol in good yield by reduction of an optically active piperitone, the goal of the present work, is not likely to be realised without a great deal more spade-work.

The striking progress in the elucidation of the constitution of the sesquiterpenes recorded in last year's Report³⁷ has been well sustained. The only known aliphatic sesquiterpene alcohols are nerolidol and farnesol, both of which have now been synthesised by Ruzicka starting from geraniol.³⁸



³³ Chem. Soc. Trans., 1923, 123, 2916.

³⁴ Nature, 1923, 112, 639.

³⁵ B.P. 189,450; J., 1923, 743A.

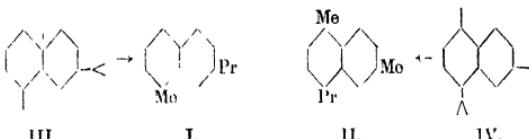
³⁶ Perf. Essent. Oil Rec., 1923, 14, 378, 415.

³⁷ Ann. Repts., 1922, 7, 496.

³⁸ Helv. Chim. Acta, 1923, 6, 492; J., 1923, 680A.

Nerolidol is used in perfumery as a fixative for more volatile odoriferous perfumes; its synthesis has been covered by patent and is being worked commercially.³⁹

The same author has advanced strong evidence that the sesquiterpenes are closely related and are built up from three isoprene skeletons, shown by the dotted lines in the formula for nerolidol. Many of them on boiling with sulphur give one of the two naphthalene hydrocarbons, eudalene (I) or cadalene (II), the carbon



III.

I.

II.

IV.

skeletons giving rise to these being called the cadinene type (IV) or the eudesmol type (III); α - and β -selinenes from oil of celery belong to the eudesmol type, as both have now been converted⁴⁰ into eudalin, and the same applies to α -santalol and α -santalene. Caryophyllene⁴¹ from oil of cloves or hops does not at present fall into this scheme, nor does the new sesquiterpene *d*-longifolene discovered by J. L. Simonsen.⁴²

One of the first examples of the use of sulphur for dehydrogenation was its action on abietic acid with production of the hydrocarbon retene (I). L. Ruzicka and F. Balas have now shown that *d*-pimamic acid gives a hydrocarbon⁴³ which is probably a dimethylphenanthrene (II). The large group of pine resin acids is thus coming under control in just the same way as the sesquiterpenes.



I.

II.

A number of interesting constituents of essential oils have been recorded during the past year. F. Rochusen⁴⁴ has examined the phenolic and acidic portion of camphor oil accumulated by Schimmel und Co., and finds 4-ethylguaiacol in the phenolic portion and hexoic, octoic, and citronellic acids in the ratio 1 : 25 : 22, in the acidic portion. A. R. Penfold and F. B. Morrison⁴⁵ have isolated a new phenol ether, C₁₁H₁₂O₃, croweacin, from the essential

³⁹ *Perf. Essent. Oil Rec.*, 1923, 14, 299.

⁴⁰ L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1922, 5, 923; *J.*, 1923, 162A.

⁴¹ E. Deussen, *Z. angew. Chem.*, 1923, 38, 348; *J. Chem. Soc.*, 1923, i., 813.

⁴² *Chem. Soc. Trans.*, 1923, 123, 2642; *J.*, 1923, 1247A.

⁴³ *Helv. Chim. Acta*, 1923, 6, 677; *J.*, 1923, 1247A.

⁴⁴ *J. prakt. Chem.*, 1922, 105, 120; *J.*, 1923, 1043A.

⁴⁵ *Perf. Essent. Oil Rec.*, 1923, 14, 258.

oil of *Eriostemon Crowei*, in which it occurs to the extent of 90%. It has an odour of safrole and is isomeric with myristicin. 4-Methoxyresorcyaldehyde, with an odour resembling vanillin, has been isolated from the roots of *Decalepis Hamiltonii* by M. G. S. Rao and M. S. Iyengar.⁴⁶ This substance was also isolated many years ago⁴⁷ by E. Goulding and R. G. Pelly⁴⁷ from an allied species of chlorocordon. Two isomeric sesquiterpene alcohols, α - and β -fusanol, isomeric with the two santalols, have been isolated by B. S. Rao and J. J. Sudborough from West Australian sandalwood oil.⁴⁸

ANÆSTHETICS.

General Anæsthetics.—Brief mention was made in last year's Report⁴⁹ to recent claims by Cotton in Canada, and Wallis in this country, that pure ether is not an anæsthetic. Cotton ascribed the anæsthetic properties to the presence of ethylene or carbon dioxide, whilst Wallis attributed it to ketones "middle members of the series," and as a result of his researches introduced "ethanesal." Such surprising statements and claims have, during the past year, been submitted to close experimental examination. R. L. Stehle and W. Bourne⁵⁰ prepared ether by the interaction of sodium ethoxide and ethyl iodide, and after purification found that such ether had in the highest degree the anæsthetic properties usually attributed to it. The present writer, in collaboration with H. H. Dale and C. F. Hadfield,⁵¹ has also prepared perfectly pure ether distilling between 34·1° and 34·15° at 751 mm. in perfect agreement with the value 34·5° at 760 mm. recorded in the careful work on ether of Wade and Finnemore.⁵² Such ether tested on animals by Dale and on human patients by Hadfield induced anaesthesia smoothly and easily, and maintained it just as do the best commercial anæsthetic ethers. An examination of various batches of "ethanesal" showed that it contained 95·5% of ether, 4% of normal butyl alcohol, and a trace of an aldehyde boiling near the recorded boiling point of butyric aldehyde. There was no evidence of the presence of ketones. Similar conclusions have been arrived at by W. Storm v. Leeuwen,⁵³ who at the request of a Dutch firm investigated the question of pure ether anaesthesia. He found that ethers of various degrees of purity differed little in their narcotic action, and pure diethyl ether prepared from the

⁴⁶ *Perf. Essent. Oil Rec.*, 1923, 14, 2, 300; *J.*, 1923, 948A.

⁴⁷ *J.*, 1908, 354.

⁴⁸ *J. Inst. Sci.*, 1923, 5, 163; *J.*, 1923, 575A.

⁴⁹ *Ann. Repts.*, 1922, 7, 498.

⁵⁰ *J. Amer. Med. Assoc.*, 1922, 79, 375.

⁵¹ *Lancet*, 1923, i, 424.

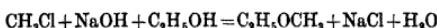
⁵² *J. Chem. Soc.*, 1909, 95, 1854.

⁵³ *Rep. Intern. Physiol. Congr., Edin.*, 1923.

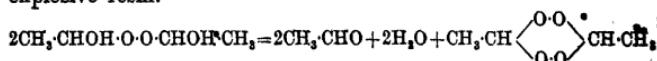
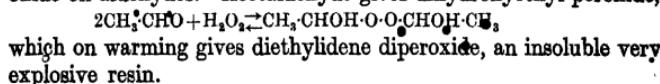
ether of crystallisation of benzidine had also the same narcotic action.

Of considerable interest to ether manufacturers are some fundamental observations of J. B. Sanderens⁵⁴ on the catalytic dehydration of alcohols by dilute sulphuric acid. A mixture of propyl alcohol, 100 c.c., and sulphuric acid, 75 c.c., boils at 140° and give mainly propylene, but with only 40 c.c. of sulphuric acid the boiling point is 125°, and 30% of propyl ether is produced. This favourable lower temperature can also be maintained by using 300 c.c. of dilute sulphuric acid corresponding to H₂SO₄.4H₂O and the yield of propyl ether is 40%. Similar considerations apply to the preparation of the ethers from ethyl, isopropyl, butyl, isobutyl, and isoamyl alcohols, the proportion of acid required to produce a certain result decreasing as the boiling point of the alcohol increases. In the preparation of methyl ether from methyl alcohol the effective hydrate is H₂SO₄.2H₂O and the boiling point of the mixture 160°-165°.

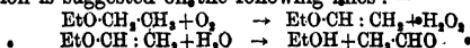
A different process for the preparation of normal and mixed ethers has been patented by C. B. Carter and A. E. Coxe⁵⁵ in the United States. The process depends on the interaction of an alcohol under pressure with an aliphatic monohalide in the presence of caustic soda, the yield being almost theoretical with pure alcohol.



The important and much-discussed problem of the autoxidation of ethyl ether seems to be nearing solution, although complete agreement has not yet been attained. In 1922 Clover⁵⁶ assigned the formula C₂H₅-O-CHMeOOH to the peroxide formed from ether by the direct absorption of oxygen, and adduced evidence that hydrogen peroxide is not a primary product of the oxidation of ether. H. Wieland and A. Wingler⁵⁷ have approached the problem by a different route, from a study of the action of hydrogen peroxide on aldehydes. Acetaldehyde gives dihydroxyethyl peroxide,



The authors have shown that dihydroxyethyl peroxide is identical with the oxidising substance found in ether residues, and its formation is suggested on the following lines:—



⁵⁴ Comptes rend., 1923, **176**, 813; 177, 15; J., 1923, 860A.

⁵⁵ U.S.P. 1,259,177; J., 1923, 851A.

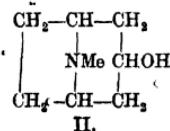
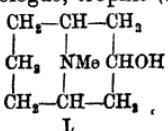
⁵⁶ J. Amer. Chem. Soc., 1922, **44**, 1107; J., 1922, 519A.

⁵⁷ Annalen, 1923, **431**, 301; J. Chem. Soc., 1923, i, 850.

the acetaldehyde and the hydrogen peroxide reacting, as shown previously, with formation of dihydroxyethyl peroxide.

Considerable progress has been made with two new general anaesthetics, ethylene and acetylene. Ethylene, a commercial product retailed in cylinders, has been used in 106 surgical cases as a general anaesthetic with complete success, by A. B. Luckhardt and J. B. Carter⁵⁸ in the United States. It is administered with about 18% of oxygen and has the advantage over nitrous oxide in that anaesthesia can be maintained without signs of asphyxia and with complete muscular relaxation. Similar results are recorded in Canada by W. E. Brown and V. E. Henderson.⁵⁹ In Germany a similar state has been reached in respect of acetylene. Pure acetylene dissolved in acetone under pressure is marketed by Boehringer under the name "narcylene." Owing to the characteristic odour of the pure material it is masked by perfumes⁶⁰ such as geraniol, or oil of pine, and any traces of acetone carried over during its use as an anaesthetic are removed by bubbling through water. H. Wieland and C. J. Gauss⁶¹ record its use in 515 cases, chiefly surgical, without accident. Anaesthesia is commenced with 60% acetylene, but afterwards the concentration can be much reduced, even to 25-30%. As 3% of acetylene or 4% of ethylene mixed with air forms an explosive mixture, such concentrations must never reach open flames. This aspect of the problem of these new anaesthetics is now receiving attention.

Local Anaesthetics.—Progress in the discovery of new drugs proceeds in two directions, the modification of chemical structures of known physiological action and the more difficult production of entirely new chemical types bearing no recognisable similarity of structure to known types, but still possessing the physiological property under consideration. The publications of the past year in local anaesthetics are illustrative of this in a greater or lesser degree. Benzoyl or substituted benzoyl derivatives of amino-alcohols as a rule show some local anaesthetic action. G. Tanret⁶² has prepared the O-benzoyl, *p*-amigobenzoyl, and cinnamyl esters of N-methyl-granatoline (I), and finds generally that the local anaesthetic actions are more marked than those of the derivatives of the lower ring homologue, tropine (II),



⁵⁸ *J. Amer. Med. Assoc.*, 1923, **80**, 765, 1440.

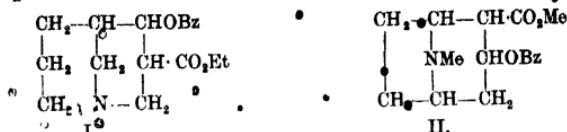
⁵⁹ *Rep. Intern. Physiol. Cong.*, *Edin.*, 1923,

⁶⁰ *E.P.* 205,240; *J.*, 1923, 1199A.

⁶¹ *Klin. Woch.*, 1923, **2**, 113; C. H. S. Horwitz, *Lancet*, 1923, **i**, 619.

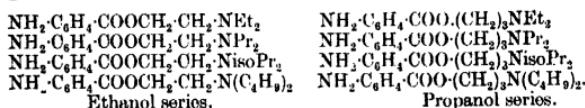
⁶² *Comptes rend.*, 1923, **176**, 1659; *J.* 1923, 855A.

whereas R. Adams and S. M. McElvain⁶³ find that the isogranatinine analogue (I) of cocaine (II) is a toxic, weak anaesthetic producing incomplete anaesthesia of the rabbit's cornea in 2% solution.



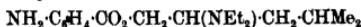
A patent⁶⁴ has been applied for, for the production of amino-benzoyl derivatives of 1-methyl-4-diethylaminopentanol-5 and 2-methyl-4-dimethylaminopentanol-5, and C. Mannich and D. Lammering⁶⁵ have described some benzoyl derivatives of β -amino-alcohols which in some cases are claimed to be more potent than cocaine. They have unfortunately an irritant action.

The relative local anaesthetic action of the series of homologues of novocaine referred to in a former Report⁶⁶ has been determined by H. L. Schmitz, E. A. Rygh, and A. S. Loevenhardt.⁶⁷ The compounds examined were



It was found that with increase of the molecular weight of the alkyl radical in both series there was a marked increase of local anaesthetic power, and members of the propanol series were slightly more anaesthetic than those of the ethanol series. The fourth member of the propanol series, "butyn," is being tried clinically, and although some reports are favourable, an adverse one by W. Hill⁶⁸ finds that it is not uniformly reliable and, unlike cocaine, does not produce the desirable property of local ischaemia of mucosal vessels.

H. Graf⁶⁹ has described the relative anaesthetic action of N-diethyl, N-diethyl, N-dipropyl, and piperidyl leucinol esters of *p*-aminobenzoic acid prepared by Karrer and his pupils. They are related to novocaine. The N-diethyl derivative



is the best, the claim being made that it is as good as, and as rapid as cocaine in its action on the cornea, and eight times as

⁶³ J. Amer. Chem. Soc., 1923, 45, 2738.

⁶⁴ Chem. Fabr. Flora, Pat. Appl.; J., 1923, 694A.

⁶⁵ Ber., 1923, 55, 3510; J. Chem. Soc., 1923, i., 43.

⁶⁶ Ann. Repts., 1921, 6, 535.

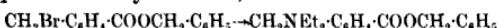
⁶⁷ J. Pharm. Exp. Ther., 1923, 21, 195.

⁶⁸ Brit. Med. J., 1923, 2, 876.

⁶⁹ Arch. exp. Path. Pharm., 1923, 99, 315.

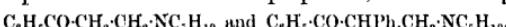
powerful as novocaine, whereas on the skin and sciatic nerve it is twice as good as novocaine. The preparation of the parent amino-alcohol, leucinol is, however, difficult.

Turning now to some new or uncommon types, β -naphthyl β -dimethylaminoethyl ether, $C_{10}H_7\cdot O\cdot CH_2\cdot CH_2\cdot NMe_2$, is stated to have a local anaesthetic action,⁷⁰ and likewise the products of the interaction of diethylamine, dimethylamine, and piperidine with benzyl *p*-bromomethylbenzoate,⁷¹ thus :—

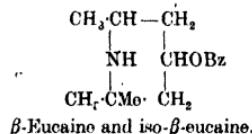
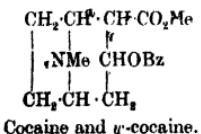


Some mixed basic esters of phthalic acid have been patented, as for example the methyl diethylaminoethyl ester of phthalic acid, $C_6H_4(CO_2Me)\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, and the 1,4-dichloro derivative. These are claimed to be powerful anaesthetics.⁷² It will be recalled that the symmetrical diethylaminoethyl phthalate, $C_6H_4(CO_2CH_2\cdot CH_2\cdot NEt_2)$, prepared by Pyman was inactive.⁷³

Some basic benzoyl compounds which are not esters⁶⁵ have been found to possess local anaesthetic properties, as for example :—



Of great interest are the results of the examination by R. Gottlieb⁷⁴ of the relative local anaesthetic action of *d*- and *l*- ψ -cocaines and of *dl*- and *l*-cocaines, which are the methyl esters of the diastereoisomeric bases benzoyl- ψ -ecgonine and benzoyl-ecgonine respectively. The stereochemistry of this pair is now almost complete, as the Chemischen Fabrik E. Merck have resolved synthetic ψ -cocaine into its enantiomorphs, which were placed at the service of Gottlieb, and have apparently resolved synthetic cocaine, as shown by a recent patent application.⁷⁵ Gottlieb found that on the sciatic nerve of the frog the order of anaesthetic power was *d*- ψ -cocaine>*dl*- ψ -cocaine>*l*-cocaine>*dl*-cocaine, whereas on the rabbit's cornea the sequence was *l*-cocaine>*d*- ψ -cocaine>*dl*- ψ -cocaine>*dl*-cocaine. In both cases the missing *d*-cocaine would appear to be the least anaesthetic member of the series.



⁶⁵ Brit. Dyestuffs Corp., W. H. Perkin, and C. R. Clemo, E.P. 193,618; J., 1923, 425A.

⁷⁰ Hoffmann-La Roche, Swiss Patent, 93,500, 93,501; J. Chem. Soc., 1923, i, 925.

⁷¹ Meister, Lucius, und Brüning, G.P. 371,046; J., 1923, 1101A.

⁷² J. Chem. Soc., 1908, 93, 1793.

⁷³ Arch. exp. Path. Pharm., 1923, 97, 113; Z. physiol. Chem., 1923, 130, 374; J., 1923, 1197A.

⁷⁴ Maeder, Merck, and Wolfs, E.P. Appl.; J., 1923, 1112A.

An exactly parallel series to this has been examined by the present writer,⁷⁶ who has resolved β -eucaine and iso- β -eucaine, the benzoyl derivatives of the diastereoisomeric α - and β -vinylidiacetonalkamines respectively, and has isolated the four possible optically active forms. The relative local anaesthetic actions were determined by J. H. Burn, who found them all equally potent on the rabbit's cornea, but on the sciatic nerve *d*, *l*, and *dl*- β -eucaines were approximately equal in action but superior to *d*, *l*, or *dl*-iso- β -eucaines, which among themselves were also equal in action. The toxicity of the β -eucaine members was less than the iso- β -eucaine members, and that of *d*- β -eucaine less than that of *l*- β -eucaine. The most favourable substance, therefore, from the point of view of anaesthesia and of toxicity is *d*- β -eucaine.

HYPNOTICS.

The two groups of hypnotics in which there is the greatest experimental activity are the urethane group and the barbituric acid group. In the former R. Willstätter and W. Duisberg⁷⁷ have prepared trichlorourethane, $\text{CCl}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$, which has been marketed under the name "voluntal." It has been examined pharmacologically by W. Straub, who summarises it as a facile, chemically harmless sleep-producer, and clinically by A. Hauptmann, who recommends it as a mild sleep-producer without disagreeable after-effects.⁷⁸ In lower doses it is sedative. The parent alcohol, $\text{CCl}_3\cdot\text{CH}_2\cdot\text{OH}$ is of interest, as it is now prepared in 70% yield by phytochemical reduction⁷⁹ of chloral by yeast, a process originally used by C. J. Lintner and H. Lüers.⁸⁰ L. Yoder⁸¹ has prepared substituted chlorourethanes of a more complex type. Methyltrichloromethylcarbinol urethane, $\text{CCl}_3\cdot\text{CHMe}\cdot\text{O}\cdot\text{CONH}_2$, and dimethyltrichloromethylcarbinol urethane, $\text{CCl}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{CONH}_2$, had a strong hypnotic action. Some related derivatives without halogen are the subject of a patent by Poulen Frères,⁸² who have prepared phenylethylcarbinol urethane, $\text{EtPhCH}\cdot\text{O}\cdot\text{CONH}_2$, phenylpropyl and phenylbutylcarbinol urethanes. The ethyl ester of *p*-ethoxyphenylmalonic acid, $\text{EtO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, although not a urethane, is like urethane an amide and an ester. It is said to be a valuable hypnotic.⁸³ An attempt to combine the sedative properties of bromo-compounds with

⁷⁶ H. King, *Chem. Soc. Trans.*, 1924, 125, 41; *Chem. and Ind.*, 1923, 1212.

⁷⁷ U.S.P. 1,427,506; *J. Chem. Soc.*, 1926, i., 10; Bayer und Co., G.P. 358,125; *J. Chem. Soc.*, 1923, i., 86.

⁷⁸ *Münch. med. Woch.*, 1922, 69, 1651.

⁷⁹ R. Willstätter and W. Duisberg, *Ber.*, 1923, 56, 2283.

⁸⁰ *Z. physiol. Chem.*, 1913, 88, 122.

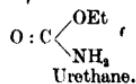
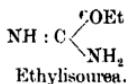
⁸¹ *J. Amer. Chem. Soc.*, 1923, 45, 475; *J.*, 1923, 329A.

⁸² F.P. 532,464; *J. Chem. Soc.*, 1923, i., 1007.

⁸³ *Akt.-Ges. f. Apilinfab.*, G.P. 371,692; *J.*, 1923, 685A.

urethane is seen in the substituted acetylallophanic ester, Et₂CBr-CO-NH-CO-NH-CO₂Et, prepared by the action of bromo-diethylacetyl isocyanate on urethane. Such compounds are said to be valuable as soporifics and sedatives.⁸⁴

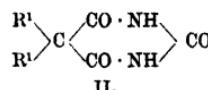
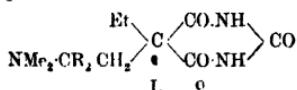
Some iso-urea derivatives which bear a superficial resemblance to urethane have been prepared and examined by S. Easterfield.⁸⁵



The following compounds were tested:—Ethylisourea, N-acetyl ethylisourea, N-benzoylethylisourea, 2-ethoxybarbituric acid, 2-ethoxymethyluracil, and carbethoxyethylisourea, EtO-CO-NH-C(OEt): NH, but with the exception of the last named were devoid of hypnotic properties.

As a result of the great attention that has recently been devoted to the barbituric series of hypnotics, practically the whole of the possible variations among the simple alkyl derivatives have been prepared. A number were referred to in last year's Report⁸⁶ and the maximum activity was found in compounds containing eleven or ten carbon atoms in all, the activity being about three times that of veronal. C. Sommaire⁸⁷ has prepared the methylbutyl, methyliisobutyl, methylisoamyl, propylbutyl, propylisobutyl, propylisoamyl, and butylisobutyl barbituric acids, but none was superior to the C₁₀ and C₁₁ series of Tiffeneau.⁸⁸ To these may be added propylisopropyl, isopropylbutyl, and isopropylisoamyl barbituric acids prepared by H. A. Shonle and A. Moment.⁸⁹

The replacement of the alkyl groups by aryl or basic groups leads to disappearance of hypnotic action as in I and II,



where R is H⁸ or CH₃ and R¹ is phenoxy, hydroxyphenyl, or a hydroxytolyl group. This is probably not surprising, as the whole character of the molecule is altered.⁹⁰

The narcotic action of symmetrical pinacones, R₁R₂-COH-COH-R₁R₂ is well-known. M. Tiffeneau and H. Dorlencourt⁹¹ have

⁸⁴ Bayer und Co., U.S.P. 1,424,236; J., 1923, 683A.

⁸⁵ J. Pharm. Expt. Ther., 1923, 20, 451.

⁸⁶ Ann. Repts., 1922, 7, 501.

⁸⁷ Bull. Soc. Chem., 1923, 38, 189; J., 1923, 328A.

⁸⁸ Ibid., 1923, 38, 183; J., 1923, 328A.

⁸⁹ J. Amer. Chem. Soc., 1923, 45, 243; J., 1923, 242A.

⁹⁰ A. W. Dox and L. Yoder, J. Amer. Chem. Soc., 1922, 45, 1754; 1923, 857A.

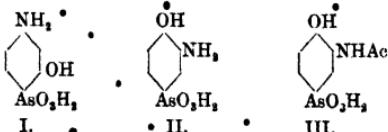
⁹¹ Comptes rend., 1923, 176, 1343; J., 1923, 625A.

prepared a number of unsymmetrical members and tested their activity by measuring the concentration necessary to produce immobility of fish. The following are described, with their effective concentrations added:—

| | | | |
|-----------------------------|-----------|-----------------------------|-----------|
| Ph-CHOH-CH ₂ OH | 1/1000; | Ph-CHOH-CMe ₂ OH | 1/1000; |
| Ph-CHOH-CMeEtOH | 1/2000; | Ph-CHOH-CEt ₂ OH | 1/7500; |
| Ph-CHOH-CFr ₂ OH | 1/20.000; | Ph-CHOH-CBu ₂ OH | 1/50.000. |

ORGANO-METALLIC COMPOUNDS.

Arsenic Compounds.—A feature of this section of the report is the sustained interest shown in arsenicals, particularly in France and in the United States. Whilst Ehrlich and his co-workers concentrated their final efforts on the arseno, -As=As-, type of linkage, French workers have more recently developed the parent pentavalent arsinic acids. E. Fourneau, A. Navarro-Martin, and M. and Mme. Trefouel⁹² have attempted to do in the arsinic acids what Nicolle and Mesnil⁹³ did in the benzidine colouring matters, the fore-runners of Bayer 205. The former authors have examined the action, on experimental trypanosomiasis, *T. brucei*, in mice and spirillosis in fowls, of a large number of phenylarsinic acids, many of which were already familiar from the results of the German school. The series comprise the isomeric amino- and hydroxy-phenylarsinic acids, some diamino and triamino acids, some isomeric hydroxyamino and diaminohydroxy acids, the acetyl derivatives of the preceding, some urethanes of *p*- and *m*-aminobenzamides of atoxyl, the corresponding ureas and the amides themselves. The best substance for the cure of trypanosomiasis in small animals was 4-amino-2-hydroxyphenylarsinic acid (I), but on experimental syphilis in the rabbit it was inferior to 3-amino-4-hydroxyphenylarsinic acid (II). The stable N-acetyl derivative (III) of this latter acid has been introduced into commerce under the name "stovarsol." It proved very effective in fowl spirillosis and it has recently been shown to act prophylactically when taken by mouth against syphilis in the rabbit, in the monkey and in man,⁹⁴ and against yaws in the monkey and in man.⁹⁵ In both cases in man volunteers were infected with massive doses of the parasites of



⁹² Ann. Inst. Pasteur, 1923, 37, 551; J., 1923, 1097A.

⁹³ Ibid., 1906, 20, 417, 519; Ann. Repts., 1921, 6, 537.

⁹⁴ C. Levaditi, L. Navarro-Martin, L. Fournier, L. Guenot, and A. Schwartz, Ann. Inst. Pasteur, 1922, 36, 729; C. Levaditi and A. Navarro-Martin, Comptes rend., 1922, 174, 893.

⁹⁵ G. Baermann, Arch. Schiffs. Trop. Hyg., 1923, 27, 229.

syphilis or of yaws after oral administration of stovarsol with completely harmless results. It is also stated⁹⁶ to have cured cases of amoebic dysentery.

Many arsenicals are known to affect the optic tract. A. G. Young and A. S. Loevenhart⁹⁷ in America have attempted to correlate chemical constitution of phenylarsinic acids with this defect, and come to the conclusion that the amino group in the *para*-position to the arsinic acid group is responsible, whilst the amino group in the *meta*-positions is harmless. This does not, however, agree with clinical experience. To quote only one instance, Beurnier and P. Clapier⁹⁸ have successfully treated 16 cases of yaws with *p*-hydroxy-*m*-aminophenylarsinic acid but only at the cost of very grave disturbances of vision.

A very suggestive communication has appeared on the mechanism of the action of arsenic on protoplasm. It will be recalled that C. Voegtlin and his co-workers have previously⁹⁹ put forward very strong evidence in support of the view that the real toxic and active constituent in the aromatic arsenicals is the oxide form RAsO, which can be produced *in vitro* or *in vivo* by reduction of the arsinic acids or oxidation of the arseno compounds. C. Voegtlin, C. S. Leonard, and H. A. Dyer¹⁰⁰ have now found that sulphur compounds, such as glutathione, thioglycollic acid, thiolactic acid, and others, counteract the toxic action of 3-amino-4-hydroxyphenylarsine oxide on trypanosomes *in vivo* in rats or *in vitro*. The theory is therefore advanced that arsenic in the form -AsO is a specific poison for the -SH group of glutathione or other possible -SH compounds in protoplasm. In other words, the death of the cell is due to interference with the oxidative processes governed by glutathione;



The condition, as laid down by Ehrlich, which a successful chemotherapeutic reagent should fulfil, is that it should have a maximum lethal action on the parasite and a minimum lethal action on the tissues of the host. This can be reconciled with the view put forward by the American workers by assuming that although the arsenic oxide combines with the thiol groups of glutathione contained in the trypanosomes and in the tissues of the host, the possibility of renewal and recuperation is more limited in the case of the trypanosome than in the case of the cells of the host.

New arsenical medicaments which have attracted attention are neosilver salvarsan and salvarsan glucoside. The former was introduced by W. Kolle,¹⁰¹ and is prepared by mixing silver salvarsan

⁹⁶ E. Marchoux, *Bull. Inst. Pasteur*, 1923, **21**, 525.

⁹⁷ J. Pharm. Exp. Ther., 1923, **21**, 197.

⁹⁸ *Trop. Dis. Bull.*, 1923, **20**, 181.

⁹⁹ C. Voegtlin and H. W. Smith, *J. Pharm. Exp. Ther.*, 1920, **15**, 475.

¹⁰⁰ U. S. Public Health Rep., 1923, **38**, 1882.

¹⁰¹ *Deut. med. Woch.*, 1922, **48**, 17.

with neosalvarsan, when a product is obtained which, unlike the reactants, is stated not to increase in toxicity on exposure to air and gives no precipitate on passing carbon dioxide. This latter property is probably a colloidal phenomenon of mutual protection, analogous to the protection of silver chloride and silver oxide by salvarsan, recently shown by W. H. Gray¹⁰² to be a largely predominating factor in the constitution of silver and sodium silver salvarsan. Kölle's product is said to be as good as silver salvarsan, but has only one half the toxicity. It has been tried clinically in an immense number of cases with, on the whole, favourable results. Salvarsan glucoside, discovered by L. Anderson¹⁰³ in England and marketed by a British firm, has also been described independently in greater detail by A. Aubry and E. Dormoy¹⁰⁴ in France. It is recorded by these latter workers as a yellow powder, soluble in water with slow hydrolysis, as is shown by a fall in its optical rotation. It is stabilised by excess of glucose, probably a mass effect, and according to A. Luguet¹⁰⁵ and to Anderson has only one-half the toxicity of neosalvarsan when administered intravenously to mice.

Aliphatic arsenicals have not hitherto attained the marked success of the aromatic derivatives. Numerous workers are, however, now developing the aliphatic field. Arsenoacetic acid, $\text{AsO}_3\text{H}_2\cdot\text{CH}_2\cdot\text{COOH}$ is the subject matter of a patent¹⁰⁶ in the United States, whilst the reduction product, arsinoacetic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{As}:\text{As}\cdot\text{CH}_2\cdot\text{COOH}$, has been described recently by C. S. Palmer.¹⁰⁷ Some allied products have been patented by Poulen Frères and C. Oechslin¹⁰⁸ in $\text{AsO}_3\text{H}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ and similar substances, but in none of these cases have therapeutic results been given. Allyl arsenate, $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{AsO}_3\text{H}_2$, has been shown by H. Ritz¹⁰⁹ to give good results in experimental trypanosomiasis in small animals comparable with those obtained with arsenious oxide.

Antimony Compounds.—Compounds of antimony, particularly tartar emetic, are important medicaments in the treatment of tropical diseases. During the past year a number of cases are recorded of the cure of ulcerating granuloma by tartar emetic.¹¹⁰ L. G. Rowntree and J. J. Abel¹¹¹ tried an analogous compound,

¹⁰² *Chem. Soc. Trans.*, 1923, **123**, 635; *J.*, 1923, 473A.

¹⁰³ *Chem. and Ind.*, 1923, 55, 345.

¹⁰⁴ *Comptes rend.*, 1922, **175**, 819; *J. Chem. Soc.*, 1923, i., 71.

¹⁰⁵ *Comptes rend. Soc. Biol.*, 1922, **87**, 1020.

¹⁰⁶ Bayer und Co., U.S.P. #1,445,685; *J.*, 1923, 518A.

¹⁰⁷ *J. Amer. Chem. Soc.*, 1923, **45**, 3023.

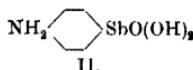
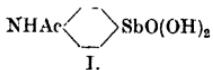
¹⁰⁸ E.P. #91,028; *J.*, 1923, 861A.

¹⁰⁹ *Arch. intern. Pharmacodyn.*, 1922, **27**, 37.

¹¹⁰ R. Onofre, *Trop. Dis. Bull.*, 1923, **20**, 286; B. B. Beeson, *ibid.*, 286; H. Goodman, *ibid.*, 287; K. M. Lynch, *ibid.*, 287.

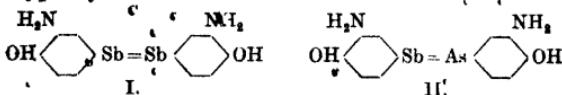
¹¹¹ *J. Pharm. Exp. Ther.*, 1910, **2**, 101.

sodium antimony thioglycollate, and the triamide of the corresponding acid in experimental trypanosomiasis and found them as efficient as other antimonials. A. Randall¹¹² has recently tried these two compounds for ulcerating granuloma with brilliantly curative results, the claim being made that in contrast to tartar emetic there was no toxic effect. Numerous attempts have been made to eliminate or to reduce the toxicity of tartar emetic by the preparation of other salts instead of the potassium salt.¹¹³ Such a procedure does not seem likely to have any permanent success. Of the numerous salts prepared by R. G. Fargher and W. H. Gray,¹¹³ quinine antimonyl tartrate had the least immediate toxicity, being five times less toxic to mice than tartar emetic. U. N. Brahmachari¹¹⁴ has also more recently prepared a large number of such antimony compounds with a view to their use in kala-azar infections, and also finds quinine antimonyl tartrate to be one of the least toxic. Where tartar emetic has been used with more or less success attempts have been made to use aromatic antimonials such as stibenyl, the sodium salt of *p*-acetylaminophenylstibinate (I).



In the treatment of kala-azar there are a number of adverse reports on its use¹¹⁵ and an equal number of very favourable ones.¹¹⁶ Brahmachari has used¹¹⁷ the urea salt of the free base *p*-aminophenylstibinic acid (II) with success, and this is confirmed by H. E. Shortt and R. T. Sen,¹¹⁸ who found that intravenous administration cured all cases of kala-azar treated by them.

The antimony analogue (I) of salvarsan has previously been described.¹¹⁹ The mixed arsenic-antimony analogue (II) has now been prepared and patented by C. N. Myers,¹²⁰ and is said to be of therapeutic value. It is prepared by reduction of an equimolecular mixture of 3-amino-4-hydroxyphenylarsinic acid and 3-amino-4-hydroxyphenylstibinic acid.



¹¹² *J. Urology*, 1923, **9**, 491; *Chem. Abst.*, 1923, **17**, 3369.

¹¹³ *J. Pharm. Exp. Ther.*, 1921, **18**, 341.

¹¹⁴ *Ind. J. Med. Res.*, 1922, **10**, 492; 1923, **11**, 196, 393, 405.

¹¹⁵ L. E. Napier, *Lancet*, 1923, i., 280; R. Knowles, *ibid.*, i., 728.

¹¹⁶ J. Renaut, Monier-Vinard, and G. Gendrou, *Bull. Inst. Pasteur*, 1923, **22**, 181; M. Plessier, *ibid.*, 183; Klippe and Monier-Vinard, *Arch. Schiffs. Trop. Hyg.*, 1923, **27**, 218.

¹¹⁷ *Ind. J. Med. Res.*, 1922, **10**, 492; **11**, 393.

¹¹⁸ *Ibid.*, **11**, 653.

¹¹⁹ *Chem. Fabr. von Heyden*, G.P. 268,451; *J. Chem. Soc.*, 1914, i., 318.

¹²⁰ U.S.P. 1,422,294; *J.*, 1923, 682A.

To complete the analogy with neosalvarsan, the corresponding sulphonylic acid derivative has also been prepared.

ANTISEPTICS.

Bayer 205.—In a previous Report¹²¹ the subject of Bayer 205, the new trypanocide, was treated at some length. It had proved remarkably curative on experimental trypanosomiasis in small animals and was on its trial for human trypanosomiasis. Its exact chemical composition is still unknown, although what was written in a former report as to its probable nature still holds good. Much valuable evidence has been accumulated of its trypanocidal action during the past two years. Its chemical development took fourteen years,¹²² and its discovery is due to the chemists Kothe, Dressel, and Orsenbeck, whilst its chemotherapy was initially due to Röhl.¹²³ Its chemotherapeutic index, I, which is the ratio of its curative dose, C, to its maximum tolerated dose, T, on small animals is 1/160, whereas that of atoxyl is about 1/2. Unlike some other effective trypanocidal agents, the disappearance of the trypanosomes from the circulating blood is somewhat tardy, and microscopical examination of affected trypanosomes is said to show that the action of Bayer 205 is mainly to influence the process of division and thus to inhibit their multiplication. It is a remarkable substance because of the long time over which it remains active in the body. The serum of a goat, which had been treated orally with Bayer 205, cured mice infected with *T. brucei*, *equinum*, or *equiperdum* three weeks after the last oral administration.¹²⁴ It slowly passes into the urine and is still curative.¹²⁵ Experiments made on the distribution of Bayer 205 in the blood show that it is non-ultrafiltrable, but is associated with the albumin fraction of the serum proteins.¹²⁶ The case of a rabbit is recorded which after an injection of Bayer 205 remained for five months protected against repeated injections with *T. equiperdum*.¹²⁷

On domestic animals and beasts of burden its action varies. Mal de Caderas, a trypanosome infection of horses in South America, has been successfully treated with Bayer 205 by E. Migone and T. Osuna,¹²⁸ who also cured a monkey with a dose of 0·02 gram.

¹²¹ *Ann. Repts.*, 1921, **6**, 551.

¹²² *J.*, 1922, 10R.

¹²³ *Deut. med. Woch.*, 1922, **48**, 1335.

¹²⁴ M. Mayer, *Arch. Schiffs. Trop. Hyg.*, 1922, **26**, 33.

¹²⁵ M. Mayer and W. Menk, *ibid.*, 1921, **25**, 376.

¹²⁶ M. Mayer, H. Zeiss, Giemsa, and Halbwkann, *ibid.*, 1922, **26**, 140.

¹²⁷ S. Sei, *ibid.*, 1923, **27**, 384.

¹²⁸ *Trop. Dis. Bull.*, 1923, **20**, 326.

In the Malay States epidemics of surra are the bane of the horse and cattle breeders. G. Baermann¹²⁹ has cured horses in 50–75% of the cases treated, but E. Rodenwaldt and J. B. D'ouwes¹³⁰ have met with less success in the Dutch East Indies. They find it curative only in very early cases and attribute its lack of greater success to the close proximity of the toxic dose for the trypanosomes and for the horse. F. K. Kleine and W. Fischer¹³¹ have tried it on infected cattle in South Africa, but without success. On man the results are much more favourable. M. Mayer and W. Menk¹³² in Hamburg record the cure of a case of infection with *T. gambiense*, whilst G. C. Low and Manson-Bahr¹³³ in this country record the cure of 7 cases out of 9 of infections with *T. gambiense*. A case of infection with *T. rhodesiense* improved but was not cured. The German expedition headed by Kleine and Fischer, under the auspices of the British Colonial Office, has returned to Europe with claims of many successes¹³⁴; 230 patients were treated in South Africa and cured by four injections, each of one gram, of Bayer 205 when the central nervous system was not affected, but when the central nervous system was affected, a longer course was necessary. The striking nature of the cures effected leads these authors to describe them as almost "biblical cures." The complete banishment of sleeping sickness is, however, not solely a question of cure or prophylaxis, but is mainly one of organisation where sanitary measures run parallel. Finally, its curative action is not confined to trypanosomiasis, as a rapid cure of kala-azar is recorded by W. Yorke.¹³⁵

Other Antiseptics.—A number of acridine dyes have been examined in their action on experimental tuberculosis in the guinea-pig and rabbit, by M. I. Smith.¹³⁶ The series included acridine, Acriflavine, I roflavine, Acridine Yellow, 2,7-dimethyl-3,6-diamino-10-methylacridinium chloride, and Acridine Orange, as well as the silver compounds of Acriflavine and Proflavine. All inhibited very powerfully the growth of tubercle bacilli *in vitro*, but *in vivo* they had no effect.

J. B. Cohen, C. H. Browning, and collaborators¹³⁷ are continuing their investigation of antiseptics and describe an interesting series of styrylpyridines and substituted styrylquinolines prepared by

¹²⁹ *Trop. Dis. Bull.*, 326.

¹³⁰ *Arch. Schiffs. Trop. Hyg.*, 1923, 27, 305.

¹³¹ *Deut. med. Woch.*, 1922, 49, 1693; 49, 1039; *Brit. Med. J.*, 1923, 2, 777.

¹³² *Arch. Schiffs. Trop. Hyg.*, 1922, 26, 208.

¹³³ *Lancet*, 1922, ii., 1265.

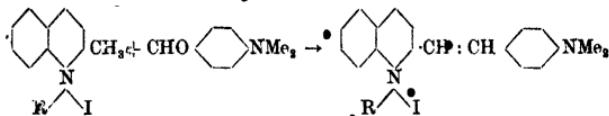
¹³⁴ *Brit. Med. J.*, 1923, 2, 777.

¹³⁵ *Trop. Dis. Bull.*, 1923, 20, 572.

¹³⁶ *J. Pharm. Exp. Ther.*, 1923, 20, 419.

¹³⁷ *Brit. Med. J.*, 1923, 2, 326.

condensation of *p*-dimethylaminobenzaldehyde with quaternary salts of quinaldines and lepidines.



For *Staphylococcus aureus* the sterilising concentration of the series lay between 1 in 200,000 and 1 in 1,000,000 in peptone water and in serum. On *B. coli* the most effective was *p*-dimethylamino-styryl-6-methylquinolinium methiodide. Some of these were tried on trypanosomiasis in mice, but unsuccessfully.

An interesting phenomenon is being studied by J. W. Churchman,¹³⁸ who found some time ago that Gentian Violet has a selective toxicity for Gram positive organisms. It is now shown that Acid Fuchsin has the opposite effect, sparing Gram positive but killing Gram negative organisms. Acriflavine has a similar action to Acid Fuchsin. A mixture of Acriflavine and Gentian Violet is effective in inhibiting the growth of bacteria at a dilution weaker than that in which either alone would be effective.

¹³⁸ *J. Exp. Med.*, 1923, **37**, 1; **38**, 1.



EXPLOSIV

By JOHN WEIR, M.A., B.Sc., Ph.D., F.I.C.,
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No outstanding advance in the manufacture or application of explosives falls to be recorded in the period under review, although the activities shown in certain directions are of considerable interest.

AMMONIUM NITRATE.

The explosion at Oppau Factory in September, 1921, caused considerable uneasiness among those interested in the storage and use of ammonium nitrate, and started a number of investigations as to the explosibility of ammonium nitrate alone and when mixed with other salts in fertiliser products. At an early stage of the inquiry the evidence indicated that the cause lay in the use of explosive for breaking up caked masses of the ammonium sulpho-nitrate, and not to any spontaneous decomposition of the material.

The explosibility of ammonium nitrate under certain conditions had been known for many years, but the strength of the initiation required to produce detonation was so great that ammonium nitrate was regarded and treated as a non-explosive. Various explosions which occurred during and after the war demonstrated that detonation of high explosives in contact with, or in the immediate vicinity of, ammonium nitrate could cause detonation.

Early in 1922 C. E. Munroe¹ published the results of an investigation of the explosibility of ammonium nitrate alone and mixed with ammonium sulphate. It was found extremely difficult to detonate a mixture of ammonium nitrate with as little as 20% of ammonium sulphate, even with 100 g. of blasting gelatin as primer, but 50 g. of the latter was sufficient to detonate ammonium nitrate alone. The explosibility increased with rise of temperature until at about 100° C. ammonium nitrate could be exploded with three No. 8 detonators. The propagation of such an explosion only takes place if the train of ammonium nitrate is of considerable cross-section, and is easily stopped by even a short gap in the train of material. Further work carried out by the U.S. Bureau of Mines indicates that ammonium nitrate becomes insensitive to detonation when pressed to densities above 1·1 to 1·3, according to the degree of confinement.

¹ *Chem. and Met. Eng.*, 1922, 28, 585; *J.*, 1922, 349A.

Before the Committee of the Reichstag P. Wöhler² reported that experts had been unable to bring about detonation of the fertiliser salts containing ammonium nitrate, and that nothing before or after the explosion had indicated any danger of explosion from them even in a state of fine division.

R. Escalas³ has suggested that some of the caked mass of the mixed salt may have contained a higher proportion of nitrate than corresponded with the 50% mixture which would render the product more sensitive.

At the request of the Dutch Government, A. J. de Weduwen⁴ carried out experiments to confirm the statement that the mixture of equal parts of ammonium nitrate and sulphate cannot be detonated. It was found that an initiating charge of 50 g. of trotyl was sufficient to effect detonation, but that a mixture containing only 30% of nitrate was very difficult to detonate completely.

These investigations have led to special regulations prohibiting the breaking up by explosives of set masses containing ammonium nitrate, but the National Research Council, Washington,⁵ has decided that ammonium nitrate when stored by itself in wooden receptacles, and apart from explosive substances, is, for transportation and storage, not an explosive.

H. Kast,⁶ in a comparison of the velocity of detonation of ammonium nitrate and ammonium perchlorate, states that the results obtained with the former are much below the theoretical value. He affirms that even with powerful initiation it does not detonate properly, but only decomposes explosively, and while obtaining values of 1200–2000 metres per sec. by experiment, he places the true value at 2800 to 4000 metres per sec., according to the density.

GUNPOWDER.

There is little of real interest to record regarding the gunpowder industry, which has been built up largely on empirical lines.

The use of sodium nitrate in place of potassium nitrate is well established, and as long as an appreciable difference in price obtains between these two substances, the cheaper sodium salt will continue in use.

A. Junk⁷ has carried out a searching investigation of the purity of synthetically prepared potassium nitrate, with a view to decide whether or not the increase in the number of explosions

² *Chem. Trade J.*, 1922, 71, 443.

³ *Chem. Zeit.*, 1921, 45, 1221.

⁴ *Z. ges. Schieß- u. Sprengstoffw.*, 1923, 18, 23.

⁵ *Chem. and Met. Eng.*, 1922, 542.

⁶ *Z. angew. Chem.*, 1923, 38, 72; *J.*, 1923, 293A.

⁷ *Z. ges. Schieß- u. Sprengstoffw.*, 1922, 17, 1; *J.*, 1922, 158A.

experienced in black powder manufacture in Germany during the war, could possibly be explained by the use of this quality of nitrate in place of that usually produced from Chile saltpetre. It seems that early in the war, when supplies of the Chile salt failed, the necessary potassium nitrate was made to a limited extent from Norwegian calcium nitrate and potassium carbonate. Later, at one factory, synthetic nitric acid was neutralised with caustic potash produced electrolytically. The main process, however, which is also in use now, entailed the production of sodium nitrate from electrolytic caustic soda and synthetic nitric acid, and the subsequent double decomposition with potassium chloride in the usual way. Junk found that the potassium nitrate prepared by the use of synthetic nitric acid is actually purer than that obtained from Chile saltpetre. In connexion with the explosions referred to, no suspicion could fall on the new type of potassium nitrate.

A new development in the method of firing black powder is described by T. W. Bacchus.⁸ A length of cordeau detonant is placed along the charge of black powder and ignites it at a rate higher than that of many dynamites. Field trials show that in this way black powder may be used in quarry blasting instead of 30%, 35%, and even 45% dynamites, and in place of ammonium nitrate dynamites, with a saving of 30% in cost. A patent has been applied for.

NITROGLYCERIN.

Two historical accounts of the manufacture of nitroglycerin have been given by R. Naoum,⁹ in which he describes the progress of the industry from time of its birth up till the present day. In particular he advocates the use of underground buildings, formed after the manner of a tunnel, as opposed to the normal practice of using buildings surrounded by large earth moulds. He maintains that actual experience has shown that these buildings are very efficient in localising the effects, should an explosion occur; also they offered greater protection from lightning and fire. With this type of building it is necessary to perform the nitration, separation, and washing of the product in the same building, and therefore each unit must be a small one. A small unit is useful in the sense that, should an explosion occur, the loss of output is small; but, on the other hand, since the number of small units must necessarily be greater, the risk of explosion is correspondingly increased. Again, the cost of manufacture tends to be very much higher with the small-unit type of plant.

Most explosives factories have, on occasions, experienced trouble due to the nitroglycerin failing to pass the Abel heat test, and

⁸ Explosives Engineer, 1923, 33.

⁹ Z. angew. Chem., 1922, 35, 461; 1923, 36, 67.

although suggestions to account for this have been made from time to time, the matter has never been properly elucidated. In an interesting paper F. A. F. Crawford¹⁰ has now shown that the low heat tests are due to an impurity in the nitric acid used for nitration purposes. The impurity was isolated as an oil from the nitric acid, and was shown to be composed of tetranitromethane, monochlorotrinitromethane, dichlorodinitromethane, with possibly a trace of chloropicrin. This oil was present to the extent of about 0.005% of the nitric acid. One part of this oil in 20,000 parts of nitroglycerin lowered the heat test from 16 to 5 min. The ingredients of the oil which were active in lowering the heat test were tetranitromethane and monochlorotrinitromethane, the latter causing most trouble in manufacture, owing to the difficulty of washing it out of the nitroglycerin by the usual process. The formation of this oily impurity is due to the presence of chlorides and organic matter in the sodium nitrate used for the manufacture of the nitric acid, and traces of chloronitromethanes are probably present in most samples of commercial nitric acid. In a previous report, it was mentioned that E. A. White¹¹ considered that the low heat tests of nitroglycerin were caused by iodine in the mixed acid, but no direct evidence was published to prove that it was the iodine and not other substances which caused the lowering of the heat test. It may be mentioned that iodine is readily removed from nitroglycerin by the washing process, and is therefore not likely to cause heat-test trouble, and moreover low heat tests given by samples containing iodine can be readily distinguished from the normal low tests by the fact that the dry portion of the test paper also becomes discoloured.

F. Blechta¹² has isolated trimethylene-glycol from glycerin produced by the fermentation process, and has given particulars of the dinitrate, which was readily obtained. This substance has been known for a considerable time. It is a mobile liquid resembling nitroglycerin in sensitiveness and power, and, unlike nitroglycerin, it has the very useful property of not freezing at temperatures as low as -20° C. Particular care is required in the nitration of trimethylene-glycol, and Blechta blames this substance for several mishaps which occurred during nitration of fermentation glycerin in the war period. Trimethylene- and ethylene glycol dinitrates together with the nitration products from ethylene¹³ and ethylene oxide¹⁴ are all open to the same objections, namely, they are more volatile than nitroglycerin, an

¹⁰ J., 1922, 321T.

¹¹ Ann. Repts., 1920, 5, 535. J. S. Afr. Assoc. Anal. Chem., 1919, 2, 7 J., 1919, 795.

¹² Z. ges. Schieß- u. Sprengstoffw., 1922, 17, 57; J., 1922, 44A.

¹³ G.P. #38,056; J., 1921, 640A.

at present they can hardly be produced at a price which can compare favourably with that of nitroglycerin.

There has been a discussion on the explosion point of nitroglycerin, and it has been shown by H. Staudinger¹⁵ that the results may vary greatly according to the method employed. A. Stettbacher¹⁶ suggests that the purity of the substance may have a considerable effect. H. Kast¹⁷ in an interesting article explains clearly why differences must necessarily occur with different methods. Kast points out the distinction between "Entzündungs Temperatur" or explosion point, meaning the temperature at which an explosion occurs when the substance is heated, as opposed to the "Detonation Temperature" or the temperature to which the products of decomposition are raised by the explosive reaction. These expressions are frequently loosely applied, and it would be advisable if these definitions were adhered to.

NITROCELLULOSE.

There is nothing which calls for comment in connexion with the development of nitrocellulose for explosives. The main outlet for this material is for propellant powders, for which there has naturally been little demand during the past few years. What demand there was has probably been met to a great extent from war stocks. This may explain the dearth of developments in this field.

PROPELLANT POWDERS.

During the period under review no outstanding advance is to be recorded in the general manufacture of propellant powders, possibly due to a great extent to the reason referred to above. Further, in view of the fact that general investigations in connexion with military propellants are mostly confined to the military establishments of the various Powers, it is not to be wondered that so little information becomes public: on the other hand, the manufacture of propellants for sporting purposes has reached a stereotyped condition in which any radical change is governed by the difficulties in effecting cheaper production by utilisation of any other than existing processes and products.

The question of components used has received a considerable amount of attention, however, and in this connexion reference may be made to the development of the streamline bullet, both in this country and in America, and the considerable amount of literature that has sprung up around this subject.

Internal ballistics, that happy hunting ground of the theorists

¹⁴ G.P. 376,000; J., 1923, 954A.

¹⁵ Z. angew. Chem., 1922, 35, 657.

¹⁶ Ibid., 1923, 36, 60.

¹⁷ Ibid., 1923, 36, 402.

and mathematicians, has had its fair share of attention. Special mention might be made of an interesting paper by J. B. Henderson and H. R. Hassé.¹⁸ While the authors avoid arbitrary assumptions as to the relation between pressure and volume behind the projectile in the gun, application is made to the problems of internal ballistics of recent advances in the thermodynamics of dissociation and in the thermodynamics of the variation of the specific heats of gases with temperature. The whole indicator diagram of the gun can now be calculated from the chemical composition of the propellant combined with a table of heats of formation from the elements of the propellant and its products, and one set of laboratory experiments to determine the rate of burning of the propellant and its variation with pressure. Data are given for cordite Mk. I and cordite M.D. The complete theory was put to severe test during the war with very satisfactory agreement between theory and practice.

On the subject of the ballistics of shot-gun powders an admirable series of articles has appeared in *The Field*.¹⁹ These give a comprehensive survey of the functioning of shot-gun powders and components, and afford an instructive insight into a subject about which very little appears in the general literature of ballistics.

Manufacture.

M. F. Chase,²⁰ in an article describing the design, construction and operation of the U.S. Government Explosives plant in Vancouver, tabulates the operations for producing 625,000 lb. of nitrocellulose powder per 24 hours. The article contains, among other points, an account of the purification and nitration of the cellulose used, and a short sketch of the powder plant.

A series of articles appeared in the *Mémorial des Poudres* embracing certain features of nitrocellulose powder production. One of these articles²¹ describes certain modifications which have been made in powder presses for the purpose of eliminating waste and improving the quality of the product. In connexion with the question of pressing, Ab der Halden²² gives an account of an investigation of the relations existing between the plasticity of "poudre B" paste, its content of nitrocellulose, soluble and insoluble in ether-alcohol, and the quantity of solvent used in producing it. It is stated that for any given percentage of soluble nitrocellulose a minimum quantity of solvent must be

¹⁸ *Proc. Roy. Soc.*, 1922, A 100, 461; *J.*, 1922, 199A.

¹⁹ *Field*, 1923, 141, 900, 926, 992; 142, 8, 196, 203, 269, 274.

²⁰ *J. Ital. Phys. Chem.*, 1922, 14, 260.

²¹ *Mém. Poudres*, 1922, 20, 164.

²² *Ibid.*, 1922, 20, 154; *J.*, 1923, 204A.

used to obtain a satisfactory plasticity. Above this minimum increase in plasticity is proportional to quantity of solvent. The plasticity of a paste considered as a function of the quantity of solvent present is said to increase more rapidly the greater the percentage solubility of the nitrocellulose. It may be remarked here that a great deal of valuable information would be likely to be gained by a thorough investigation of the extrusion of plastics. The very interesting work that is being carried out in the United States on the plasticity of clays would appear to have a considerable bearing on the extrusion factors arising in the manufacture of, in particular, powders, both of the single and double base type. In a further article dealing with the manufacture of "poudre B",²³ it is stated that the viscosity of the powder paste must lie within certain limits in order that the subsequent pressing may prove satisfactory. A suitable measure of the viscosity has been found in the coefficient of plasticity, which is defined as the distance in mm. to which a cylinder of 10 mm. diameter sinks in 1 minute under a load of 2 kg. into a compact block of paste. An apparatus for this determination is described. Experiments are tabulated showing the satisfactory control of mixing for "poudre B" before pressing.

With regard to the question of drying powder, G. Weissenberger²⁴ gives data for the time of drying, maximum air temperature, and weight of recovered solvent, in the case of the manufacture of the Austrian powders, M.93, M.93a, and M.12. The solvent employed in the first two cases is a mixture of acetone and alcohol, and in the third case a mixture of acetone and ether.

L. Butin²⁵ describes a method for the economy of steam and time in the drying of nitrocellulose powder which has been subjected to the ordinary warm water soaking process subsequent to solvent recovery. The material is loaded into a hexagonal rotating drum, direct from the water steeping. The drum is fitted with grid-like sides, and when loaded with the warm wet powder it is rotated, the heat contained in the powder being thus utilised for the drying of the grain.

In connexion with the surface moderation of powders, H. Marqueyrol²⁶ describes an investigation dealing with gelatinisers and their most important properties. A list is given of gelatiniser patents which have appeared since 1900, and the gelatinisation of certain nitrocottons by alcoholic solutions of various types of gelatinisers, including substituted ureas, esters, and cyclic ketones, is described.

²³ *Mém. Poudres*, 1922, 20, 146; *J.*, 1923, 204A.

²⁴ *Z. ges. Schieß- u. Sprengstoffw.*, 1921, 16, 169, 179; *J.*, 1922, 80A.

²⁵ *Mém. Poudres*, 1922, 20, 345; *J.*, 1923, 204A.

²⁶ *Ibid.*, 1921, 19, 150; *J.*, 1922, 349A.

Powder Forms and Characteristics.

Much of the work published in this connexion deals with a comparison of the double-base powders, that is containing both nitroglycerin and nitrocellulose, with the single-base or pure nitrocellulose type. Generally speaking, it may be said that investigators are striving to improve the double-base powders from the point of view of erosion and muzzle flash, and the single-base powders from the point of view of ballistic stability under moist climatic conditions. In this connexion the papers by J. R. Mattern,²⁷ L. C. Weldin,²⁸ E. Chevereau,²⁹ and T. L. David³⁰ may be consulted.

Numerous references have appeared during the period under review to the development in the United States of a smokeless, flashless, non-hygroscopic powder.³¹ It is stated that satisfactory powders of this nature have been produced for 4-in. Stokes mortar and for 75-mm. field gun. For the former the powder is a thin perforated disc which requires no bag or container to prepare it for firing : the 75-mm. powder is in the form of thin strips, making it easy to handle or load. The method of manufacture is briefly outlined. The powder can be fired within 48 hours of the time of mixing, but most uniform ballistics are obtained after 2 3 days' ageing. Though not quite smokeless, it is said to produce no more smoke than the present service powders. A similar powder is being developed for the 155-mm. Howitzer ; it is said to contain a small percentage of nitroglycerin. In the supplementary volumes of the Encyclopaedia Britannica³² the composition of an American flameless propellant is given as 60% of nitrocellulose, 25-28% of nitroglycerin, 5-7% of diethyl phthalate, 3-5% of neutral potassium tartrate, and mineral jelly up to 5%. In the same article it is stated that the stabiliser found in powder used in German 77-mm. field guns is dimethyldiphenyl-thiourea.

It will be remembered that in previous years reference was made to the introduction of tin or tin oxide into powders for the reduction of metallic fouling in rifles. Experimental trials of such powders were made in England without very much success being attained, and it is interesting to note that apparently the use of such powders in the United States is being abandoned,³³ it being now considered more advisable to use a special alloy for the jacket

²⁷ *Arms and the Man*, 1923, 450.

²⁸ *Army Ordnance*, 1923, 342.

²⁹ *Mép. Poudres*, 1922, 20, 168, J., 1923, 204A.

³⁰ *Army Ordnance*, 1921, July and August.

³¹ *Ibid.*, 1923, 282, 320. *Chem. and Met. Eng.*, 1922, 60, *Times*, June 23, 1923.

³² Lt.-Col. F. M. Richard, vol. 32, p. 196.

³³ *Arms and the Man*, April, 1922.

of the bullet. T. Wheleⁿ,³⁴ in an article on the qualities desired in bullets, says that transferring the tin as a coating to the bullet jacket gave good accuracy, but that subsequently the top of the rifle lands was found to have been badly eroded by the tin. This is much in accordance with British experience. He also corroborates the statement that introduction of tin or tin alloy into the powder is not a success.

In the realm of shot-gun powders, a great deal of prominence has been given to the use of du Pont No. 93 powder for game cartridges equivalent to the British 12-bore 2½-in., and the small bores.³⁵ The powder is a nitrocellulose powder surface-modulated to give the progressive burning action desirable for these cartridges, and may be regarded as a new type for this purpose. Powders giving the same effect have been developed in France, though they differ in nature from the American powder. The patterns given by the American powder in what are known as Super X cartridges are very good, but the powder is not adapted for existing standard British 12-bore 2½-in. cartridges which form by far the greater bulk of the cartridges loaded in Great Britain.

Experiments have also been carried out in France³⁶ with the well-known French shotgun powder "poudre T." This powder, with a slight alteration in the granulation, has been found to give more constant loads, a defect from which the older powder suffered.

Stability.

The question of testing the stability of powders seems a matter of perennial investigation, but a sure and rapid test as to how a powder will behave under varied climatic conditions is still awaited. In fact, from the nature of the problem it is very doubtful that such a test which will be generally applicable will ever be devised. Still the search goes on, but it may be said generally that unless the test results are correlated with the behaviour of the powder under various service conditions, these results are of little value.

M. Briotet³⁷ states that the mode of action of the quartz mercury lamp is distinct from that of the natural agents at work during ordinary storage. Further, considerable chemical variations follow slight modifications of the causative factors, and there is no suitable method of measuring the radiating power. Under the conditions adopted by Berthelot, which appear difficult to

³⁴ *Field and Stream*, July, 1922.

³⁵ C. Askins, *Ibid.*, Sept., 1922. *Arms and the Man*, Dec., 1921, and Jan. and Feb., 1922.

³⁶ M. Porché, *Mém. Poudres*, 1922, 20, 300; *J.*, 1923, 265A.

³⁷ *Ibid.*, 1921, 19, 185; *J.*, 1922, 349A.

modify, exact measurements are impossible, and the apparatus is condemned. The nature of the gases obtained from various types of French powder is described. An investigation concerned with the inflammation temperature of powders is described by A. Koehler.³⁸ Determinations carried out in air, *in vacuo*, and in carbon dioxide, show that with rapid heating the atmosphere has no influence on the inflammation temperature. It is concluded that no useful purpose would be served by storing B Powder *in vacuo*.

J. D. Berkhout³⁹ gives an account of the methods employed in the Artillery Laboratory, Hambrug, Holland, for determining the stability of smokeless powders. The test consists essentially of a determination of loss of weight in definite times at various temperatures, and a note of the time at which red fumes appear. It thus bears a close resemblance to certain German tests.

Solvent Recovery.

The question of solvent recovery plays such an important part in the economies of powder production that any development in connexion with the subject may be legitimately regarded as a fit subject for comment. It may be taken that the older methods of recovery such as scrubbing with water or bisulphite, refrigeration methods, or even the more recent sulphuric acid absorption process have become out of date, and that the methods of the future lie between the Bregeat cresol absorption process and the adsorption processes which employ activated charcoal or the various inorganic gels. Strong claims are put forward for both the cresol and the adsorption processes, and the relative merits are the subject of many and often contradictory remarks. In the explosives industry the Bregeat process established itself very firmly during the war. Whether the rapid strides that are being made in the adsorptive qualities of charcoal will result in the displacement of the cresol process is a matter upon which no sure opinion can yet be given.

An instructive and interesting article on the technology of solvent recovery by means of activated charcoal, as carried out in the Bayer factories, is contributed by H. Carstens.⁴⁰ The article describes the entire process of solvent absorption, solvent recovery, and charcoal regeneration.

The raw materials to be used as sources for activated charcoal have been the subject of comment,⁴¹ and the lignites, anthracite, and cannel may be employed under certain conditions.

³⁸ *Mém. Poudres*, 1921, **19**, 138; *J.*, 1922, 348A.

³⁹ *Z. ges. Schieß- u. Sprengstoffw.*, 1922, **17**, 33; *J.*, 1922, 310A.

⁴⁰ *Chem.-Ztg.*, 1921, **45**, 524; *J.*, 1921, 613A.

⁴¹ *Brennstoff-Chem.*, 1922, **3**, 241; E. R. Sutcliffe, *J.*, 1922, 202A.

An important feature of the use of absorbents, particularly in explosives manufacture, is, of course, the fire hazard, and W. D. Milne⁴² discusses the question from this point of view. It is considered that no single feature is more likely to cause fire than generation of static electricity.

T. W. Wild⁴³ gives an account of the methods of volatile solvent recovery used in cordite manufacture, using sulphuric acid, water, or cresol as absorbing media. The distillation processes are outlined and the factors governing efficiency are noted.

Methods of recovery involving the use of water, sodium bisulphite and heavy tar oils are described by P. Brasseur.⁴⁴ Particular attention is devoted to the absorbent action of sulphuric acid and cresol. The relative efficiencies of the various processes are discussed and curves are supplied showing the percentage of solvent vapour recovered by the absorbent from atmospheres containing various amounts of solvent vapour. The statement that adsorption processes cannot compete with those utilising suitable absorbents seems scarcely established. Among the patents that may be referred to as covering the use of adsorbents for the recovery of solvent vapour are the proposal by R. Lambert⁴⁵ to use iron oxide gel, and that of L. Hamon and T. H. Eyrom⁴⁶ to treat peat, lignite, sawdust, and the like for conversion into charcoal for use in the recovery of solvent vapours.

E. R. Sutcliffe and H. S. Raper⁴⁷ have taken out a patent for the use of steam superheated to 300° C. for the recovery of solvent adsorbed by activated charcoal.

HIGH EXPLOSIVES FOR MILITARY PURPOSES.

In the realm of military high explosives no new products have come to light during the period under review. As in most branches of the heavy chemical industry, development work follows the line of investigation of the underlying principles of the processes of manufacture, or the introduction of refinements into the existing methods. This is supplemented to some extent by the accumulation of data regarding the properties of the various products, but in general over the whole subject a condition of relative stagnation may be said to exist.

Picric Acid.

The manufacture of this explosive, despite the recognised advent of trinitrotoluene, still holds a firm position, particularly in

⁴² *Chem. Age (New York)*, 1923.

⁴³ *Ibid.*, 1923, 207.

⁴⁴ *Fed. Ind. Chim. Belg.*, 1922, 155.

⁴⁵ E.P. 188,786; *J.*, 1923, 39A.

⁴⁶ E.P. 187,971; *J.*, 1923, 706A.

⁴⁷ E.P. 188,723; *J.*, 1923, 83A.

France, has been investigated further by M. Marqueyrol and P. Lorette.⁴⁸ In previous years it will be remembered that a high degree of sulphonation of the phenol, prior to conversion into picric acid, was recommended. The authors here further stress the point that the temperature of nitration be maintained sufficiently long at 110° to transform into picric acid all the dinitrosulphonate.

The nitration of phenol has also been closely investigated by R. King,⁴⁹ who has studied the nitration of various phenolsulphonic acids and nitrophenylsulphonic acids. He comes to the conclusion that to obviate formation of oxalic acid and dinitrophenol, the latter of which shows great resistance to further nitration by diluted acids, it is essential to carry out the sulphonation under conditions similar to those of Marqueyrol.

The production of picric acid from various tree gums is an investigation which seems to recur at intervals. Most of such processes are, of course, uneconomic. W. R. Jewell⁵⁰ describes methods for oxidising and nitrating grass tree gum, and for separating and purifying the picric acid so obtained. The highest yield obtained was from *Xanthorrhaea hastilis*.

The hygroscopicity of picric acid has been investigated by L. G. Marsh.⁵¹ He shows that the hygroscopicity is dependent on the purity of the material, or on the presence of water-soluble products. Material containing 0·05% SO₃, as free sulphuric acid or sulphate, in an atmosphere saturated at 32° C., increased in weight by almost 2% in 48 hours; material containing 0·16% SO₃ increased 5%.

T. S. Patterson⁵² describes a method for the determination of sulphuric acid in picric acid, based on the extraction with water of a benzene solution of the material and titration of the aqueous extract.

The use of chlorine or bleaching powder for decolorisation of picric acid wash waters and effluent has been patented by J. Klemenz.⁵³

Trinitrotoluene and Amato.

R. Robertson⁵⁴ describes investigations at Woolwich during the war, which led to improvements in manufacture and purification of trinitrotoluene. Points dealt with are methods of nitrating mononitrotoluene; purification of crude T.N.T. by washing or crystallising from alcohol and by treatment with sodium sulphite;

⁴⁸ *Mém. Poudres*, 1921, 18, 1.

⁴⁹ *Chem. Soc. Trans.*, 1921, 119, 2105; *J.*, 1922, 120A.

⁵⁰ *Chem. Eng. Min. Rev.*, 1921, 18, 322.

⁵¹ *J. Ind. Eng. Chem.*, 1922, 14, 32; *J.*, 1922, 141A.

⁵² *J.*, 1923, 21T.

⁵³ G.P. 347,011 and 348,058; *J.*, 1922, 271A, 393A.

⁵⁴ *Chem. Age*, 1923, 451.

detoluuation of waste acid ; determination of the purity of T.N.T. from its setting point ; trouble caused by impurities. It is stated that common symmetrical T.N.T. has lower explosive power than some of its isomerides, but it is more stable. W. H. Gibson⁵⁵ gives an account of the proportions of M.N.T., D.N.T., and T.N.T. produced at each stage of nitration of toluene, and the behaviour of the crude T.N.T. under various conditions is investigated. As a factor of importance in connexion with manufacturing control, a special method is described for the analysis of M.N.T. based on the fusion curves of (*o* and *p*) and (*m* and *p*) M.N.T.'s. Ternary setting point diagrams are also constructed for mixtures of 2.3, 3.4, and 3.6 D.N.T.'s. Finally, the trinitration of M.N.T. was studied and a ternary fusion diagram for crude T.N.T. constructed. From this a curve is derived giving the change of crystallisation point during the nitration of toluene. The eutectic mixtures of the isomeric T.N.T.'s. were determined and results were worked out to form a ternary fusion diagram.

A great deal of controversy has ensued regarding the nature of the T.N.T. isomers occurring in T.N.T. oil. In this connexion reference may be made to the papers by M. Giua,⁵⁶ O. L. Brady,⁵⁷ M. Marqueyrol,⁵⁸ and H. Brunswig.⁵⁹ The latter states that the explosion temperatures with soda of the β and γ isomers are considerably less than in the case of the other isomers.

As bearing on the stability of T.N.T., reference may be made to tests carried out by the U.S. Bureau of Mines.⁶⁰ It is stated that material stored for 6 years does not show appreciable deterioration in stability, strength, or sensitiveness.

A patent by C. M. Stine⁶¹ covers a method for purifying T.N.T. or trinitroxyloyl by washing the crude product with carbon tetrachloride.

Tetryl (Trinitrophenylmethylnitroamine).

A paper of importance on the manufacture of tetryl is that of L. Desvergne.⁶² A bibliography and summary of existing knowledge of tetryl manufacture is given. Various methods of manufacture are compared, and it is considered that the French method is the best. The effects of incubation of tetryl at various temperatures are given ; data are recorded regarding sensitiveness to shock friction. A description is given of a continuous nitration apparatus for the production of tetryl.

⁵⁵ *Chem. Soc. Trans.*, 1922, 121, 273 ; *J.*, 1922, 274A.

⁵⁶ *Gazzetta*, 1921, 51, II, 113 ; *J.*, 1921, 715A.

⁵⁷ *Chem. Soc. Trans.*, 1922, 121, 328 ; *J.*, 1922, 393A.

⁵⁸ *Mém. Poudres*, 1921, 19, 66.

⁵⁹ *Z. angew. Chem.*, 1923, 36, 75.

⁶⁰ *Chem. Age*, 6, 428.

⁶¹ U.S.P. 1,450,675 ; *J.*, 1923, 523A.

⁶² *Mém. Poudres*, 1922, 20, 217 ; *J.*, 1923, 205A.

W. L. Tanner⁶³ describes the method of manufacture of tetryl employed at the High Explosives plant of the Bethlehem Steel Corporation. The chief feature of the process is the rather high temperature of nitration. It is claimed that with proper control crystallisation from a volatile solvent is not necessary to obtain material to pass the British Government specification. The recovery of oxides of nitrogen from the nitration and the treatment of spent acid are described.

The utilisation of monomethylaniline for the production of tetryl has been investigated by T. J. Nolan and H. W. Clapham.^{63a} The authors, employing methylphenylnitrosamine, have produced tetryl in a form which, even in the crude state, is free from *m*-nitrotetryl. The nitration, which is carried out in sulphuric acid solution, is characterised by very smooth working and in this respect forms a marked contrast to previous efforts to obtain tetryl by direct nitration of monomethylaniline. Also the use of methylphenylnitrosamine results in considerable economies in nitric acid consumption as compared with the standard method using dimethylaniline.

Miscellaneous.

A. Pomaski⁶⁴ describes the preparation of trinitro-*m*-xylene. He states that nitration can be carried out in one, two, or three stages. The three-stage process is the most economical and was in use in France, the two-stage process has not been applied in practice, and the one-stage process as worked out by Prof. Solonina was in use at the Krotte Factory in Petrograd. The molecular ratios used in the nitration are 6 of *m*-xylene, 22½ of nitric acid, and 52 of sulphuric acid, the dilution being 10½ of water. The xylene is added to the acid mixture, the temperature being kept below 50° C. by cooling. Further details of the working up of the product are given. A yield of about 75% is obtained.

A. A. Drummond⁶⁵ describes the preparation of trinitrobenzene by the nitration of dinitrobenzene under various conditions with a high temperature of nitration and a strong nitrating acid. A yield of only 29% of the theoretical was obtained, and the proportion is, of course, not an economic one. This bears out general experience on the nitration of dinitrobenzene.

L. Desvergne⁶⁶ gives a bibliography regarding the manufacture, purification, and military application of trinitroanisole and trinitrophenetole. Data are given regarding sensitiveness to shock, velocity of detonation, pressure developed in bomb tests, priming

⁶³ *Chem. and Met. Eng.*, 1923, 29, 404.

^{63a} *Sci. Proc. Royal Dublin Soc.*, 1923, 17, 219; *J.*, 1923, 1103A.

⁶⁴ *Przem. Chem.*, 6, 330.

⁶⁵ *J.*, 1922, 338T.

⁶⁶ *Mém. Poudres*, 1922, 20, 269; *J.*, 1923, 205A.

power, etc. A discussion of the decomposition of trinitrophenetole during its preparation from dinitrophenetole is included. These explosives were much employed by the Germans, but their production never seems to have reached any dimensions in Great Britain; the substances are esters of picric acid, and as such are rather sensitive to hydrolysis. A detailed description of the method of production of trinitrophenetole is given by M. Marqueyrol⁶⁷; this covers the production of the intermediate dinitrophenetole from dinitrochlorobenzene.

A wide range of substances of possible interest as explosives, including hexanitrodiphenyl ether and hexanitrodiphenyl sulphide and sulphone, have been investigated by C. F. Van Duin.⁶⁸ The problem of stability to heat is discussed, and the various tests in vogue are criticised. Explosion temperature and sensitiveness to shock and friction are also studied.

Justrow⁶⁹ gives a theory for the construction of high explosives shell charges. In a further paper⁷⁰ he supplies an expression by which the number of fragments into which a shell may burst may be calculated. The data required are the explosive charge, the elastic limit of the shell materials, its extension, and the mean strength of the shell walls. The influence of the nature of the explosive used is represented by a factor based on picric acid as standard. Factors are given for the various high explosives. The numbers are in about the correct proportions of brisance values, but may require modification as a result of sufficient practical testing.

F. Olsen⁷¹ discusses the properties required in boosters for high explosives shells; among the boosters considered are cyclotri-methylenetrinitroamine, hexanitrodiphenylguanidine, and cyanuric triazide.

Of practical interest is a paper by C. G. Storm,⁷² who gives an account of an investigation regarding sympathetic detonation of high explosive shells loaded with T.N.T. and amatol, with a view of determining safe conditions for storage. It was found that detonation is transmitted laterally to much greater distances than in a "nose-to-nose" direction, and that a concrete floor or the confinement offered by the walls and roof of a building has no material effect on the transmission of sympathetic detonation. The author concludes that for the storage of shells small magazines of a cheap, light type should be used, spaced at distances which will preclude the transmission of detonation from one to another.

⁶⁷ *Mém. Poudres*, 1921, **19**, 70; *J.*, 1922, 349A.

⁶⁸ *Rec. Trav. Chim.*, 1920, **38**, 145; *J.*, 1920, 676A.

⁶⁹ *Z. ges. Schieß- u. Sprengstoffw.*, 1922, **17**, 84.

⁷⁰ *Ibid.*, 1922, **17**, 36.

⁷¹ *Army Ordnance*, 1923, 269.

⁷² *Ibid.*, 1923, 256.

R. Robertson and W. E. Garner⁷³ have devised a bomb for the measurement of the heat evolved during the detonation of high explosives, and of the volume of gases produced, and the conditions of loading and initiation have been standardised. Experiments have been carried out with T.N.T., picric acid, and amatol 80/20. In the case of an explosive giving complete combustion, the results for heat of detonation and composition of products agree with those deduced theoretically. The products of detonation of high explosives in vacuum include CO₂, CO, H₂O, H₂, CH₄, C₂H₂, NH₃, HCN, carbon, and a trace of NO₂, but the proportions are dependent on factors which include density of loading, and confinement of the explosive, its completeness of detonation, and the nature of the initiator. The conditions under which free carbon is produced are discussed, and it is shown that its formation is accompanied by an increase in the heat of detonation and a diminution in the volume of gases liberated. Increase of density and confinement of the explosive give greater deposition of carbon during cooling. Incomplete explosion leads to increase in the volume of nitric oxide produced.

HIGH EXPLOSIVES FOR CIVIL PURPOSES.

Gelatins.

There is nothing of outstanding importance to record regarding developments in the pure gelatin class of explosives. One interesting feature is the production of plastic gelatinous ammonium nitrate explosives by the use of aqueous solutions introduced by the Dynamit A.-G. vorm. A. Nobel u. Co. and P. Naumann. In the original patent⁷⁴ a concentrated solution of a salt containing water of crystallisation, preferably calcium nitrate, was used to the extent of 3% to increase the plasticity of ammonium nitrate safety explosives which contained insufficient nitroglycerin-nitrocotton gelatin to render them sufficiently soft for cartridgeing. This was followed by a similar claim⁷⁵ for concentrated sulphite-cellulose waste liquor. Still more recently the claim has been extended to cover a solution of any soluble salt added to the explosive.⁷⁶

Powder Explosives.

In this class also little of note has appeared. Most of the new explosives are slight variations of older compositions with different proportions or with the addition of a small proportion of another oxidant or nitro-compound.

⁷³ Proc. Roy. Soc., 1923, A103, 539; J., 1923, 803A.

⁷⁴ E.P. 140,446; J., 1921, 28A.

⁷⁵ G.P. 353,200; J., 1922, 839A.

⁷⁶ E.P. 189,780; J., 1923, 999A.

Determined efforts in the United States to utilise the large stock of surplus propulsives remaining from the war have led to the development of numerous compositions,⁷ consisting mainly of low-grade dynamites of approximately 40% strength which may contain anything from 20% to 90% of ground nitrocellulose powder, or cordite, from 0 to 60% of sodium nitrate, with other ingredients such as aluminium and nitroglycerin to increase sensitiveness. Similar compositions, but containing ammonium nitrate as well, have also been produced. Such explosives, among which are the Dumorites, have a wide field of usefulness in America, where low-grade explosives are used for opening up and clearing new country.

A. J. Strane⁷⁸ patents the method of utilising waste propulsive powders such as cordites by mixing them in a granulated form with blasting powder, by which means an explosive of much higher power than the blasting powder is obtained.

The supply of high explosive recovered from shells etc. is not yet completely exhausted, and such explosives as amatol are still being utilised for various purposes. The recovery processes have not been without their accidents. L. Wöhler⁷⁹ gives an account of a disastrous explosion, in Stolberg, of two wagons of an artificial manure which had been prepared by mixing two parts of ammonal with three parts of kainite. It is presumed that the original explosive was badly mixed, and that a portion more sensitive than the rest, when struck with a pick in the presence of sand, detonated.

In consequence of the frequent explosions which occurred in the working up of mixtures of ammonium nitrate and T.N.T. recovered from munitions, the Chemische Technische Reichsanstalt investigated the ease of ignition and explosibility of these mixtures and of T.N.T. alone. The igniting compositions used contained stated amounts of black powder, petro-klastit, and aluminium powder. With somewhat more powerful ignition than that effected by fuse alone, explosive actions of the black powder type occur with both mixtures of ammonium nitrate and T.N.T. in powder form and with loose T.N.T., the effect varying with the degree of confinement. Under special conditions foreign bodies, such as detonators, left in the recovered explosive may lead to detonation of the mixture.

W. O. Snelling⁸⁰ patents the treatment of a wet organic nitrate such as nitrostarch with a saturated solution of ammonium nitrate, the excess of solution being removed. The water is thus replaced

⁷⁷ U.S.P. 1,447,218; J., 1923, 426A. U.S.P. 1,411,674; J., 1923, 393A.
U.S.P. 1,420,384; J., 1922, 649A.

⁷⁸ U.S.P. 1,455,309; J., 1923, 745A.

⁷⁹ Z. angew. Chem., 1923, 36, 85; J., 1923, 293A.

⁸⁰ U.S.P. 1,395,776; J., 1923, 206A.

by a solution containing very little water, and it is claimed that by subsequent admixture of the treated organic nitrate with oxidising salts, useful blasting explosives are produced.

Chlorate Explosives.

The toxicity of the fumes from chlorate explosives has been investigated by H. Kast and A. Haid.⁸¹ The explosives tested were some of the commoner German compositions of this class, such as Miedziankit, Gesteinsalbit, Gesteinskoronit, etc., the compositions of which are given. The fumes were obtained both by detonation and by burning, and the tests were arranged to detect acidity, oxidising substances such as chlorine or nitrogen peroxide, and also carbon monoxide. In the detonation products chlorine and nitrogen peroxide were present only in traces, but in larger quantity in the combustion products. On the other hand, carbon monoxide was always present in the detonation products to the extent of 1 to 3%, even with explosives having excess of oxygen in their composition, but did not exceed 0.1% in the combustion products. It is pointed out that although the combustion products of chlorate explosives contain highly toxic gases, yet the combustion products of ammonium nitrate explosives are worse, in that they contain more nitrogen oxides. On the other hand, the chlorate explosives are more readily ignited.

In the development of new ammonium nitrate explosives, a small proportion of potassium perchlorate is frequently added to increase the sensitiveness of the composition to detonation and propagation. This is exemplified in numerous German explosives such as Nospagit,⁸² Ammon Cahucit, and Germanit. A. Segay⁸³ patents a composition of this nature. C. J. S. Lundsgaard and K. T. Herbst⁸⁴ suggest the use of the perchlorates of mono-, di-, or trimethylamine or tetramethylammonium, in admixture with other materials, to give blasting explosives. It is difficult to see how these explosives could have any special advantage or compare in price with other perchlorate explosives.

Safety Explosives.

Very little advance has been made as regards safety explosives during the last two years. In Great Britain a number of new explosives have appeared on the "Permitted list",⁸⁵ but they are mostly slight modifications of those already on the list, taken out

⁸¹ Z. ges. Schiess. u. Sprengstoffw., 1922, 17, 145 J., 1922, 961A.

⁸² Chem. Ind., 1922, 479.

⁸³ E.P. 201,791; J., 1923, 990A.

⁸⁴ U.S.P. 1,423,233; J., 1922, 690A.

⁸⁵ Explosives in Coal Mines Orders, 1922-1923.

by newly formed companies, or compositions which have been modified for use with a No. 6 detonator.

Owing to difficulties with the supply of coal gas at Rotherham testing gallery, the official test of permitted explosives has, by arrangement with Messrs. Nobel's Explosives Co., been transferred meantime to Ardeer Factory, and preliminary experiments have been carried out at Rotherham with mixtures of methane and air, methane, hydrogen, and air, and petroleum ether and air, with a view of finding a suitable substitute for mixtures of coal gas and air. The mixture of methane and air gave charge limits for permitted explosives far higher than those in force at present, the mixture of methane, hydrogen, and air gave irregular results, while a mixture of petroleum ether and air containing 1·5 to about 1·75% of petroleum ether gave charge limits similar to those at present in force. The experiments were not continued in view of the appointment of a Joint Committee on the Testing of Permitted Explosives, and on their recommendation the research was entrusted to the Explosives in Mines Research Committee appointed in September, 1922.⁸⁶ The whole subject of explosives for use in fiery and dusty mines is being studied under this committee, which has published a memorandum⁸⁷ giving a historical sketch of the methods used in Britain and other countries for determining the "safety" of explosives and outlining a programme of work which it is proposed to carry out and which it is hoped may lead to improved types of coal mining explosives and improved methods of testing them. Much of the practical work in this connexion is being carried out at Eskmeals and Ardeer.

In Belgium a number of new safety explosives have been placed on the list of Explosifs S.G.P.⁸⁸ These explosives fall into two main classes, either with or without nitroglycerin, and closely resemble the British ammonium nitrate permitted explosives. A recent development in Belgium has been the adoption by the Government of the compulsory use of the Lemaire Safety Sheath in certain classes of coal mining. Lemaire has shown that by firing dynamite and blasting gelatin cartridges in protective sheaths composed of mixtures of certain materials, such as sodium chloride, sodium fluoride, cryolite, etc., the "safety" towards firedamp and coal dust is enormously increased. These sheaths are formed round the ordinary cartridges of safety explosives, thus conferring further safety upon explosives which have already passed the Belgian gallery test. The use of this sheath must reduce the efficiency of the explosive considerably. Patents covering various types of safety sheath useful for this purpose have been taken out by

⁸⁶ Annual Report of H.M. Inspector of Explosives for 1922, pp. 20, 21.

⁸⁷ Memorandum on Explosives for Use in Fiery and Dusty Mine, etc., 1923.

⁸⁸ Ann. Mines Belg., 1922, 300, 302, 303, 621; 623; 1923, 44, 143.

Société Anonyme d'Arendonck,⁸⁸ by G. van Troll,⁸⁹ and by J. M. Bonser.⁹⁰

As the result of the destruction of the Testing Station at Liévin the study of safety explosives in France has been resumed at a newly erected station at Montlucon.⁹² In France the "Explosifs antigrisouteux" are not submitted to any standard gallery test before authorisation, but must satisfy, *inter alia*, the conditions that no combustible products shall be produced on detonation, and that the calculated temperature of detonation must not exceed 1900° C. for explosives used in stone works and 1500° C. for those used in coal. Austria, Czechoslovakia, Belgium, Germany, Great Britain, and the United States use, as a criterion of safety, the gallery test, which is an attempt to duplicate practical conditions. This difference of view-point has been emphasised in a recent controversy between E. Audibert⁹³ of the Montlucon station and E. Lemaire⁹⁴ of the Belgian station at Frameries. Audibert⁹⁵ asserts that the increased safety conferred by the Lemaire cartridge can be produced in other ways, and is practically the same as that of a tamping equal in weight to the sheath. He also discounts the value of photographic investigation of the flame from explosives. In an examination of "Flammocite," which is identical in composition with Flammivore III bis, authorised for use for fiery mines in Belgium, Audibert⁹⁶ rejects this composition on the grounds of (1) uncertainty as to the homogeneity of the mixture, (2) presence of carbon monoxide in the explosion gases, (3) character of the explosive apart from the inert constituents. This attitude merely amounts to ignoring the value of a "safety ingredient," which all practical gallery tests have shown to be essential to safety explosives. The position is rather anomalous in that France would reject the safety explosives of other countries on grounds similar to those stated above, whereas the French safety explosives would possibly not pass the gallery tests of other countries. Audibert⁹⁷ states that "although long experience justifies the confidence that French users of explosives have in the grisou-dynamite and grisou-naphthalites authorised for use in fiery and dusty mines, the reasons why these explosives are safe are not properly understood." For this reason further investigation is continuing.

⁸⁸ E.P. 196,917.

⁸⁹ E.P. 201,507.

⁹⁰ E.P. 205,022.

⁹² E. Audibert, *Ann. Mines France*, 1922, **12**, 15.

⁹³ Loc. cit. and *Rev. de l'Ind. Min.*, 1922.

⁹⁴ *Ann. Mines Belg.*, 1922, **23**, 649.

⁹⁵ *Ann. Mines France*, 1922, **1**, 399.

⁹⁶ *Ibid.*, 1922, **11**, 317.

⁹⁷ *Memorandum on Explosives for use in Fiery and Dusty Mines, etc.*, 1923, 7.

Liquid Air Explosives.

Strenuous efforts continue to be made to extend the use of liquid oxygen explosives, but up to the present the only plants where their use has been established on a large scale and is being continued are in the Lorraine ironstone mines and at Pachuca in Mexico. In the case of the latter A. P. Akin⁹⁸ reports that liquid oxygen explosives are used only on faces which are easily accessible. R. G. Skerritt⁹⁹ reports that the first application of liquid air explosives in the United States will be made in the iron ore mines at Mineville, with a plant producing 75 kg. of liquid air per hour. To facilitate transport of the liquid air the plant will be erected 1000 ft. below the surface level.

The U.S. Bureau of Mines¹⁰⁰ has issued a report on the progress made with their investigation on liquid oxygen explosives. These experiments include absorption and evaporation tests on a number of absorbent and combustible materials, which have made it possible to design mixtures which would retain enough liquid oxygen after 15 min. for exact combustion of their combustible material to carbon dioxide and water. The Trauzl lead block test was found unsatisfactory for comparing strengths owing to the small charge used, and the ballistic pendulum was found more satisfactory, showing the liquid oxygen explosives to compare favourably with 40% dynamite in strength. Preliminary tests indicated that liquid oxygen explosives are not suitable for use in gaseous and dusty coal mines. Electric detonators are recommended as the most certain means of firing.

Under the auspices of Liquid Air, Ltd., trials were carried out in 1922 in the ironstone mines at Frodingham¹⁰¹: the results were stated to be most satisfactory, but the method has not yet been adopted. J. A. Smeaton¹⁰² gives an account of a demonstration given at Hayange in Lorraine. It is very difficult to form definite conclusions from the recent development of the position of liquid oxygen explosives in France. Previous to the imposition of a tax on these explosives in 1921 they were in a position of advantage as compared with other explosives, but the Association Minière d'Alsace et de Lorraine complain that the imposition of this tax has arrested the development of liquid oxygen installations in the iron mines. In a report¹⁰³ issued in December, 1922, they enumerate the advantages of liquid oxygen explosives as

⁹⁸ Eng. and Min. Press, 1922, 978.

⁹⁹ Compressed Air Magazine, 1923, 427.

¹⁰⁰ U.S. Bureau of Mines, Tech. Paper 294, 1923.

¹⁰¹ Colliery Guardian, 1922, 124, 1284.

¹⁰² Iron and Coal Trade Rev., 1923, 129.

¹⁰³ "L'Emploi de l'Explosif à l'Oxygène liquide dans les Mines de Fer de Lorraine."

regards safety, hygiene, and technique of usage, and point out the advantages which would accrue to the State in time of war in that nitrates would be set free for military purposes. They ask for a reduction of the tax. This report is controverted¹⁰⁴ by P. Cazeneuve,¹⁰⁵ who finds nothing in the claims to warrant a reduction. He states that all German and Polish mines which used liquid oxygen during the war have abandoned it now, and that of 68 mines in Lorraine only 11 continue to use liquid oxygen. The whole question is, however, confused by the political situation, and the necessity for fostering the artificial production of nitrates in France.

A. James,¹⁰⁶ in the course of a paper on the use of liquid oxygen in mining, gives details of experience of its use in the Real del Monte Mines at Pachuca. The advantages claimed for liquid oxygen are in general those which have already been enumerated in previous reports. W. Cullen, in remarks contributed on this paper, points out that the claim of greater safety is not substantiated, and that the cost of liquid oxygen explosives should be calculated on the whole expenditure involved. This is usually expressed in terms of the cost of the explosive, but with these explosives, which have a much lower density than the ordinary gelatinous explosives, extra labour, material, and power are involved in drilling. This increases the cost very considerably. It appears that there is a field for liquid oxygen explosives in certain classes of work and possibly in countries where explosives are imported, and the cost of transport is very high, but for general mining they do not appear to have any future.

TESTING.

A series of tests conducted by the U.S. Bureau of Mines,¹⁰⁷ relative to the effect of cartridge diameter on the strength and sensitiveness of certain high explosives, have shown that rate of detonation and sensitiveness to explosion by influence increase with the increase of diameter of the cartridge. Gelatin-dynamites decrease rapidly in both these respects on ageing, but ammonium dynamites are little affected. This decrease in gelatin-dynamites proceeds more rapidly the smaller the diameter of the cartridges, and the decrease is more rapid with 60% than with 40% low-freezing gelatin-dynamite. These results are used in an article¹⁰⁷ written to show the disadvantage of small diameter cartridges.

¹⁰⁴ "Les Explosifs dans les Exploitations Industrielles devant l'Impôt," 1928.

¹⁰⁵ "Liquid Oxygen in Mining," published by the Institution of Mining and Metallurgy, 1928.

¹⁰⁶ U.S. Bureau of Mines, Serial No. 2436.

¹⁰⁷ Explosives Engineer, 1923, 65.

It is pointed out that the percentage of paper on $\frac{7}{8}$ -in. cartridges is nearly double that on $1\frac{1}{2}$ -in. cartridges.

O. Poppenberg¹⁰⁸ has made an interesting contribution to the study of the products of explosion. It was formerly supposed that an explosive decomposes in different ways according to the loading density. As far as detonating explosives are concerned, this is incorrect, as the explosion is so rapid that the pressure produced at the moment of explosion is practically independent of the surrounding medium. However, unless these initial products of explosion are quickly cooled, secondary reactions take place, and these are dependent on the pressure and rate of cooling. Various devices were used for cooling the explosion gases quickly, such as firing the explosive in an iron bomb enclosed in a large evacuated bomb. The loss of energy entailed by the sudden expansion of the gases into a vacuum after the bursting of the bomb led to rapid cooling. In another method, double-walled vessels were used with the annular space filled with mercury or water. The gases produced by an explosive fired in the vessel were quickly and intimately mixed with the mercury or water, and rapidly cooled. Practical results obtained from experiments with picric acid and T.N.T. agreed very well with those deduced theoretically.

INITIATING EXPLOSIVES.

In spite of the new initiating explosives which make their appearance from time to time in the patent literature, mercury fulminate and lead azide are still the only two of practical importance. Fulminate has not yet been supplanted to any great extent, though lead azide is making headway.

A. Langhans¹⁰⁹ continues to publish the results of his investigations on fulminate and its manufacture, but fails to improve the long-established process which has been worked out very exhaustively on empirical lines.

R. C. Farmer¹¹⁰ carried out an interesting investigation into the decomposition of mercury fulminate at $80^{\circ}\text{C}.$, and observes that following a quiescent period, the rapid formation of a catalyst brings about a brisk evolution of carbon dioxide. This result was quite unexpected in view of the earlier observation of Hoitsema¹¹¹ that at $130^{\circ}\text{C}.$, i.e., immediately below its explosion point, mercury fulminate gives off oxygen. Farmer's promised investigation into the solid products of the decomposition will therefore be awaited with interest.

¹⁰⁸ *Z. angew. Chem.*, 1923, **36**, 80; *J.*, 1923, 293A.

¹⁰⁹ *Z. ges. Schiess- u. Sprengstoffw.*, 1922, **17**, 122, 131, 141, 150, 159; 1923, **18**, 17, 521; *J.*, 1923, 120A.

¹¹⁰ *Chem. Soc. Trans.*, 1922, **121**, 174; *J.*, 1922, 199A.

¹¹¹ *Z. physik. Chem.*, 1896, **21**, 147.

Most of the interest in new detonator work is, however, now centred on lead azide. Nobel's Explosives Co. have obtained an extension to their original patent for this country for a period of four years in view of its unavoidable suspension during the war period.¹¹²

In 1920, W. Eschbach¹¹³ patented the use of aluminium detonator tubes as containers for lead azide. More recently he has patented detonator tubes of aluminium alloy for the same purpose.¹¹⁴ He also proposes aluminium tubes as fulminate containers along with an inner protecting cap of copper, brass, or celluloid.¹¹⁵ The construction of such a detonator might actually be of commercial advantage in Germany, where copper has been scarce and high in price.

Judging from the patent literature, however, the position of lead azide as a fulminate substitute will be fiercely attacked, as an energetic search for new initiators is going on. As examples of these we may mention 4,6-dinitro-2-diazophenol,¹¹⁶ tetrazole and triazole, and their derivatives,¹¹⁷ the salts of azodithiocarbonic acid,¹¹⁸ cyanuric triazide,¹¹⁹ 1,3-dinitro-4,5-dinitrosobenzene salts,¹²⁰ and basic lead salts of nitro compounds.

Sulphuryl azide is described by T. Curtius and F. Schmidt.¹²¹

It is, of course, very doubtful whether any of the new explosives above mentioned will ever come into use. It is always long odds against the laboratory article becoming a finished commercial product, which must be at once stable, readily ignitable, good running, moderately sensitive, powerful, and cheap. These proposals are, however, of interest in that they illustrate the persistent groping for a new initiator which is going on, and also because they set forth the strategic importance of sodium azide as the base of operations. Sodium azide is prepared by the interaction of ethyl nitrite and hydrazine hydrate in presence of alkali. In this connexion R. A. Joyner and Nobel's Explosives Co.¹²² make continuous the Raschig process for the manufacture of hydrazine

¹¹² *Chem. Trade J.*, 1923, 487.

¹¹³ E.P. 151,572; *J.*, 1920, 766A. U.S.P. 1,438,309; *J.*, 1923, 121A.

¹¹⁴ E.P. 204,277; *J.*, 1923, 154A.

¹¹⁵ E.P. 195,907.

¹¹⁶ E. v. Herz, G.P. 373,426; *J.*, 1923, 864A. W. M. Dehn, U.S.P. 1,428,011 and 1,404,887; *J.*, 1922, 961A.

¹¹⁷ E. v. Herz, G.P. 370,574; *J.*, 1923, 685A. H. Rathsburg, E.P. 185,555; *J.*, 1922, 880A.

¹¹⁸ H. Rathsburg, E.P. 188,302; *J.*, 1923, 688A.

¹¹⁹ Soc. of Chem. Ind. in Basle, E.P. 170,359; *J.*, 1921, 872A. See also E. Ott, G. P. 352,223 and 350,564; *J.*, 1922, 917A; 1923, 246A. Wöhler, *Z. angew. Chem.*, 1922, 35, 545.

¹²⁰ H. Rathsburg, E.P. 190,844; *J.*, 1923, 332A. W. Friederich, E.P. 192,830; *J.*, 1923, 332A.

¹²¹ *Ber.*, 1922, 55, 1571, 1581.

¹²² E.P. 199,750; *J.*, 1923, 907A.

hydrate by the interaction of sodium hypochlorite and ammonia, and also avoid ammonia recovery.

The dry mixing of initiating explosives such as lead azide and lead styphnate involves an element of risk, which E. von Herz avoids by simultaneous precipitation of the two salts and by precipitating one upon the other in suspension.¹²³ This method has been made general in a series of patents issued by the Rheinisch-Westfälische chemists, the claim being made not merely for a safe mixing, but also for the precipitation of homogeneous crystals of isomorphous salts of a modified or increased strength. Thus, W. Friederich claims for the precipitation of lead azide with other salts,¹²⁴ H. Rathsburg for trinitrophloroglucinol,¹²⁵ and H. Rathsburg and W. Friederich for tetrazole derivatives.¹²⁶

The principle has not yet found a useful practical application, but the ground covered by the patents is so extensive that assiduous research might very probably bring to light some combination of importance. Incidentally, the individual patents reserve an enormous field.

There is nothing new in detonator construction, though the Schütze detonator, which applies the Neumann principle of the hollowed-out charge to the base of the detonator, is the subject of a prolonged and not very edifying wrangle over Bomborn's priority claims.¹²⁷ W. Eschbach also patents the application of the principle.¹²⁸

The conclusion arrived at after a perusal of these and other articles¹²⁹ must be that sound conclusions as to the initiating power of detonators cannot be derived from mechanical tests such as the lead-plate test, and that such tests can only have value when used to compare detonators of the same type. These views find confirmation in a very thorough study of the question by J. Barab.¹³⁰

With regard to developments in cap compositions, nothing of moment has been achieved. The ultimate objective here is a single loading which will possess all the desirable qualities. As yet no such substance is to hand.

J. E. Burns¹³¹ makes an interesting claim for a mixture of (1)

¹²³ E.P. 187,012; *J.*, 1922, 961A.

¹²⁴ E.P. 180,605; *J.*, 1922, 568A.

¹²⁵ E.P. 190,215; *J.*, 1923, 162.

¹²⁶ E.P. 195,344; *J.*, 1923, 804A.

¹²⁷ B. Bomborn, *Z. ges. Schieß- u. Sprengstoffw.*, 1921, 16, 177; 1922, 17,

55, 135. C. Bunge, *ibid.*, 1922, 17, 16. J. Zinzius, *ibid.*, 1922, 17, 163, 167. M. Wolf, *ibid.*, 1922, 17, 111. W. Eschbach, *ibid.*, 1923, 18, 23.

¹²⁸ E.P. 172,914.

¹²⁹ See also B. Grotte, *Chem. and Met. Eng.*, 1922, 26, 1180; *J.*, 1922, 567A.

¹³⁰ *Explosives Engineer*, 1923, 51.

¹³¹ U.S.P. 1,437,224; *J.*, 1923, 804A.

an oxidising agent leaving a corrosive residue, (2) an oxidising agent, and (3) a seducing agent with a non-corrosive residue; (2) and (3) preponderate and leave (1) inert.

H. T. Peck¹³³ claims mixtures containing, *inter alia*, styphnic acid and lead styphnate, and also a mixture containing diplumbic ditinitroresorcinol,¹³³ a substance to which, without any apparent warrant, he assigns a graphic formula double that of ordinary normal lead styphnate.

ANALYSIS.

Not the least of the problems which face the explosives chemist are those connected with the analysis of explosive mixtures. An important separation with which he is constantly faced is that of nitroglycerin and other ether-soluble nitric esters and nitro-aromatic compounds.

M. Marqueyrol and E. Goutal¹³⁴ gave two methods for the quantitative determination of mixtures of trinitroglycerin and dinitroglycol. The first is based on the observation that in a dry atmosphere over sulphuric acid, trinitroglycerin suffers no loss, while dinitroglycol loses 12 mg. per 24 hours; in the second the composition is deduced from the magnitude of the freezing point depression of benzene containing the material under examination. Although the probable interference of other substances which may be present in the ether extract of an explosive is considered, it is clear that these methods can only have a limited application.

A method for the quantitative separation of nitroglycerin and nitro-aromatic compounds is given by W. Dickson and W. C. Easterbrook.¹³⁵ The nitroglycerin is destroyed by the action of ferrous chloride in presence of methyl alcohol, which prevents the further nitration of the nitro-aromatic compounds present.

A method for determining the residual acetone in propellant powders is described¹³⁶ depending on the action of sodium hypochlorite on acetone in alkaline solution producing iodoform. The powder is cut up and hydrolysed by sodium hydroxide solution; the acetone present is distilled over into a flask, cooled if water, and the determination carried out on the distillate under specified conditions. Alcohol, aldehyde, diphenylamine, and ammonia do not interfere. The presence of substituted ureas involves a slight correction.

¹³³ U.S.P. 1,416,121 and 1,416,123; *J.*, 1922, 524A.

¹³⁴ U.S.P. 1,416,122; *J.*, 1922, 524A.

¹³⁵ *Mém. Poudres*, 1921, 19, 87; cf. *J.*, 1920, 528A.

¹³⁶ *Analyst*, 1922, 47, 112; *J.*, 1922, 310A.

¹³⁷ H. Marqueyrol, *Mém. Poudres*, 1921, 19, 150.

A method of determining the T.N.T. and tetryl content of mixtures of them, based on the relative solubilities of T.N.T. and tetryl in carbon tetrachloride at 0° C., is described.¹³⁷ The method is fairly rapid and easy, and gives results accurate to within 2%. The higher the percentage of T.N.T. present, the greater the error.

Acknowledgment is made of the valuable assistance rendered by various members of the technical staff of Messrs. Nobel's Explosives Co. in the preparation of this section of the report.

¹³⁷ C. A. Taylor and W. H. Rinkenbach, *Ind. Eng. Chem.*, 1923, **15**, 280; *J.*, 1926, 523A.

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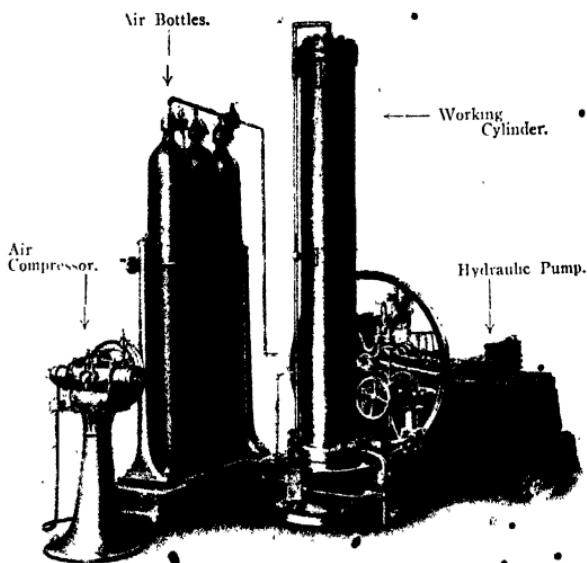
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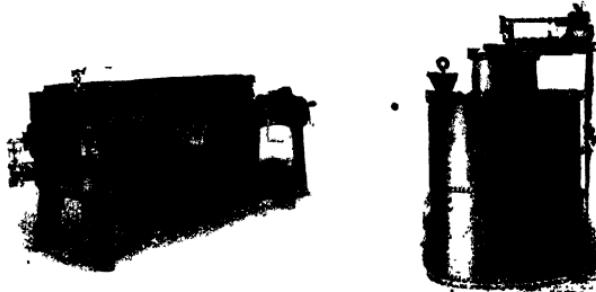
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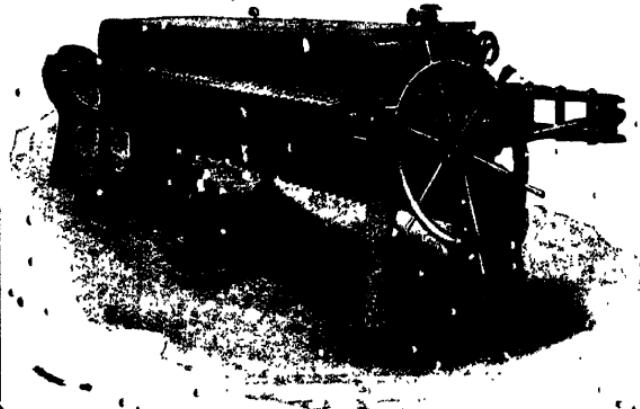
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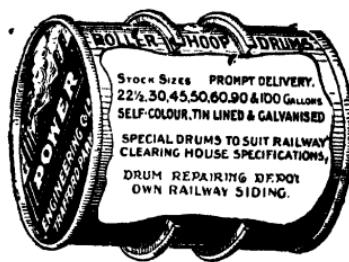
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